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Semiannual Technical Summary Report *Sept. NO. 3*

on

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prepared for
Advanced Research Projects Agency

10 Aug submitted by
Charles H. Kruger, Principal Investigator

for the period
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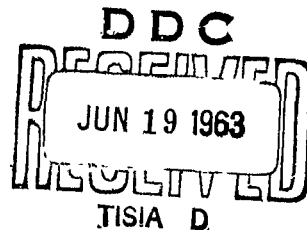
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INTRODUCTION

The present report is the third semiannual technical report written under Contract AF49(638)-1123 which is supported by the Advanced Research Projects Agency. This research effort encompasses studies of magneto-gasdynamics, fuel cell, and thermoelectric energy conversion, and involves the efforts of faculty and students in the Departments of Mechanical Engineering, Aeronautical Engineering, Materials Science, Chemical Engineering and Chemistry.

This report includes contributions by several authors, as follows:

Magnetogasdynamics

Channel

Professor C. H. Kruger

Shock Tube

Professor Daniel Bershader

Fuel Cells

Kinetic Studies

Professor David M. Mason

Chemisorption Studies

Professor Eric Hutchinson

Thermoelectricity

Basic Materials Research

Professor David A. Stevenson

Measurements at Elevated
Temperatures

Mr. S. Schweitzer

Transient Performance of
Thermoelectric Generators

Mr. Carl Moyer

I. MAGNETOGASDYNAMICS

(a) Continuous Flow Channel

Substantial progress has been made on the MGD channel program during this reporting period. While several delays have been experienced in the delivery of components by outside suppliers and fabricators, the channel program has now reached the final assembly and testing stage. With the exception of the test section, all major components including instrumentation are now in hand and functioning properly. The test section, while essentially complete, has developed leaks in the cooling water passages. We and the fabricator are, at the time of this writing, studying modifications which will correct the situation. This difficulty, while delaying somewhat the date of initial power generation experiments, seems likely to have a small effect upon the overall time schedule of the program since the time made available by this delay can be profitably used for calibration and checkout experiments.

The development of a facility of this size requires much time and effort. Until quantitative results are obtained, however, it is difficult to reflect this in a technical report without discussing the many small and relatively mundane problems and details which in fact add up to the net progress. With this in mind figures and photographs have been used freely here with the hope of giving an overall impression of the progress and present status of the program.

In the way of a brief review, the general configuration of the MGD channel is shown in Figure 1. Design details of the generator test section are shown in Figure 2. The combustion of ethyl alcohol seeded with potassium hydroxide and oxygen provides a plasma flow of up to about .3 kg/sec at a temperature in the vicinity of 3000°K. Combustion of the fuel-seed mixture takes place in a swirl type combustion chamber where nitrogen may be added to lower the flame

temperature. The plasma stream then passes through a mixing chamber, the generator test section, a diffuser, the "scrubber", and finally out through an exhaust stack. The flow dimensions of the test section are approximately 1-1/4 by 3 inches by 20 inches in length. Thirteen pairs of electrodes may be connected so as to withdraw power in the Hall, segmented, continuous, or mixed modes of operation.

During this reporting period, Dr. Stewart Way of Westinghouse Research Laboratories spent six weeks at Stanford consulting with the members of the MGD power generation program (at no cost to the contract). He offered a number of valuable suggestions based upon his experience regarding construction and operation of the channel and also made available a Westinghouse IBM 7090 program for the calculation of thermodynamic properties including conductivity of combustion products. We have now acquired this information for ethyl alcohol seeded with potassium or cesium over a range of temperatures and pressures of interest. Typical values of several of the calculated quantities are shown in Figures 3 and 4. Using these properties, a calculation has been made of the variation of performance with length in the Stanford channel. Results for the case of stoichiometric combustion with no nitrogen and 2% atomic ratio potassium seed are given in Figures 5 and 6. The total maximum power output in this case is 38.6 kilowatts. These results were obtained by an integration of the one-dimensional equations of motion, accounting for friction and magnetic forces and power output but neglecting heat transfer losses. Estimates indicate that heat transfer losses will be small but not insignificant. The corrected net power will thus be reduced somewhat from the value given here. Continued efforts will be directed to the improvement of these calculation methods, with the final goal of a programmed prediction technique.

As mentioned previously most of the major components are now in hand. The instrument and control panel is shown in

Figure 7. Measurements will initially be made of output currents and voltages, properties and flow rates of the plasma, combustion reactants, and cooling water, and quantities effecting magnet control. The loading arrangement will provide for rapid changes between various modes of operation during the course of a single run. Figures 8 and 9 show the burner, mixing chamber, diffusor, and scrubber assembled in position in the 28,000 gauss magnet.

A major part of the effort during the later part of this reporting period has been devoted to tests of the burner-mixing chamber assembly. Figure 10 is a photograph taken during one of these experiments, with the plasma exhausting from the mixing chamber into the atmosphere. These tests, which are not yet complete, have yielded information on preheat technique and durability of various types of magnesium oxide brick which will be used to line the mixing chamber and test section. In a recent test high purity bricks supplied by Norton and experimental Kaiser bricks were exposed to the flame for twenty minutes without failure. Electrode and thermocouple material has also been tested during these experiments.

In addition to the development of the combustion generator facility some time was given to the study of non-equilibrium ionization. Calculations were made which expanded on the analyses of Kerrebrock and Sutton. Estimates of times required for ionization agree with those presented by J. M. Smith at the recent Engineering Aspects of MHD Symposium but are based on somewhat different assumptions. It was also observed that the relative magnitudes of ionization potential and electron cross section of argon and seed materials are such that under some circumstances of steady state non-equilibrium ionization the optimum seed concentration might be zero. That is, the fractional ionization and conductivity of pure argon might be comparable to or greater than that of seeded argon. However, the

practical possibility of achieving such ionization may be limited by several loss mechanisms. These calculations agree with those given by Lyman, Goldstein and Heighway in their paper at the MHD Symposium.

In an effort to investigate these effects experimentally a glass generator section was made for the shock tube. Unseeded argon, heated and accelerated by a Mach 8 shock wave, passed through a 5700 gauss magnetic field. Currents and voltages were measured across a single pair of electrodes. In spite of some ambiguity arising from the Hall effect, preliminary results substantiated conductivity calculations based on elevated electron temperature.

The non-equilibrium ionization work has since been suspended. Both the theoretical and experimental studies were at a preliminary stage and not yet at a point where really useful information had been obtained. This work is mentioned qualitatively here for completeness and to outline the scope of our initial thoughts.

(b) Shock Tube

(1) Shock Tube Calibration

The shock tube commenced regular operation during October, 1962 with pressure drive, followed by the use of combustion drive around the end of 1962. The basic calibration of the tube is now essentially completed. Shock speeds were monitored by pressure and electrostatic discharge gauges. Thin film resistance gauges with a thin electrically insulating coating are being developed as alternative shock velocity gauges, but with ultimate application as wall heat transfer gauges. Test conditions reached were sufficient to produce electron concentrations of 10^{16} /cc. or larger, which is the general regime in which experimental programs will be carried out.

Preparations for high purity operation have progressed with an improved vacuum in the tube. Baking-out of the walls with heating tape and the use of a liquid nitrogen trap have

made possible vacua around 5×10^{-6} mm. Hg, with an outgassing rate of 10^{-5} mm. Hg/minute. Further improvements are under way involving the increase of pump capacity at low pressures, and a flow system for additionally increased purity.

(2) Instrumentation Development

An optical interferometer has been made available on loan and is now set up (Figure 11). Several test interferograms have been taken in connection with calibration of the light source. The light source is a major instrumentation problem in optical studies of high temperature gases; work on this problem continues. Present efforts are conceived with an exploding wire device.

To obtain the necessary resolution in time, two approaches are being followed. One is to use a fractional microsecond light source which will give a "snapshot" interferogram behind the shock wave. The other is to obtain time-resolved records of both the interferometric or spectral type with a rotating mirror camera. Such a device has been constructed from modifications of available designs. A picture is shown in Figure 12. The camera utilizes a hexagonal stainless steel mirror having faces flat to one-half wavelength. The mirror, suitably coupled to air turbine-drive motor capable of 80,000 r.p.m., sweeps an image of a desired cross sectional strip over 3 feet of film. The sweep speeds will be, typically, 5 mm/microsecond across the film. Focussing is obtained with a 3 inch diameter, f-2.5 lens. The mirror and motor have been dynamically balanced.

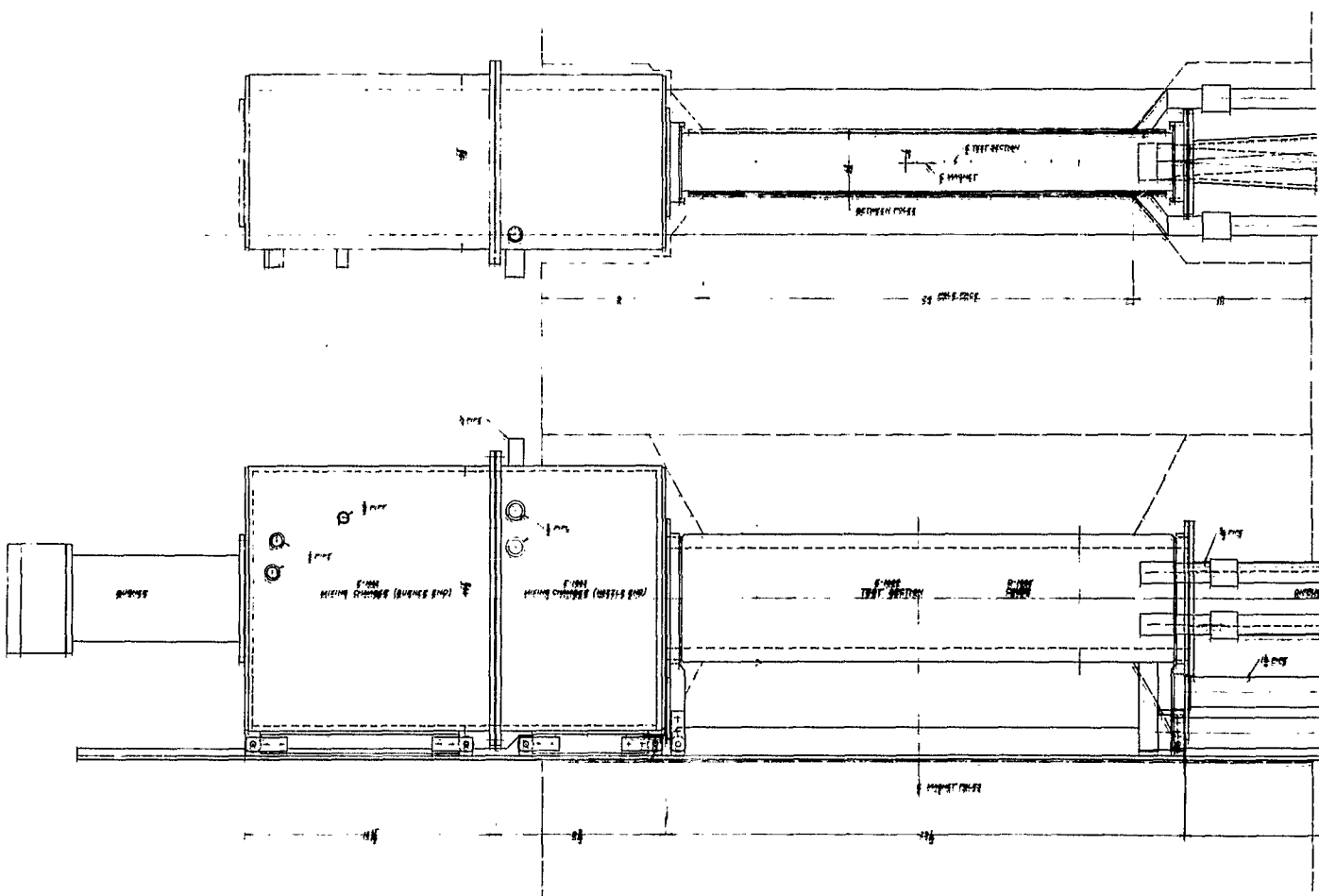
(3) Design of the Ionization Rate Experiment

Calculation leading to the design of the shock induced rate of ionization experiment in argon have so far dealt largely with equilibrium properties of species behind strong shocks in argon. There are some published data on thermodynamic properties, and for present purposes, the interest centers on the effect of variation of atom, ion

electron densities on the shift of fringes as monochromatic light is transmitted through the shock heated gas. Figure 13 shows the regime of sensitivity of the optical interferometer to equilibrium electron concentration. The dotted lines show the separate contributions of each species to the total fringe shift (solid line). The dominating influence of electrons due to their large polarizability is prominently shown.

At any given Mach number with equilibrium conditions specified by Figure 13, it is the purpose of the experiment to determine the approach to equilibrium in order to serve as a guide to the correct theoretical formulation. Various theories on the mechanism of the ionization process have been presented in the progress report of April 1962. Computations on the relaxation times of different ionization models have been made. These results will be compared with simultaneous interferometric and spectroscopic data obtained during the test.

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Figur
MGD Generato

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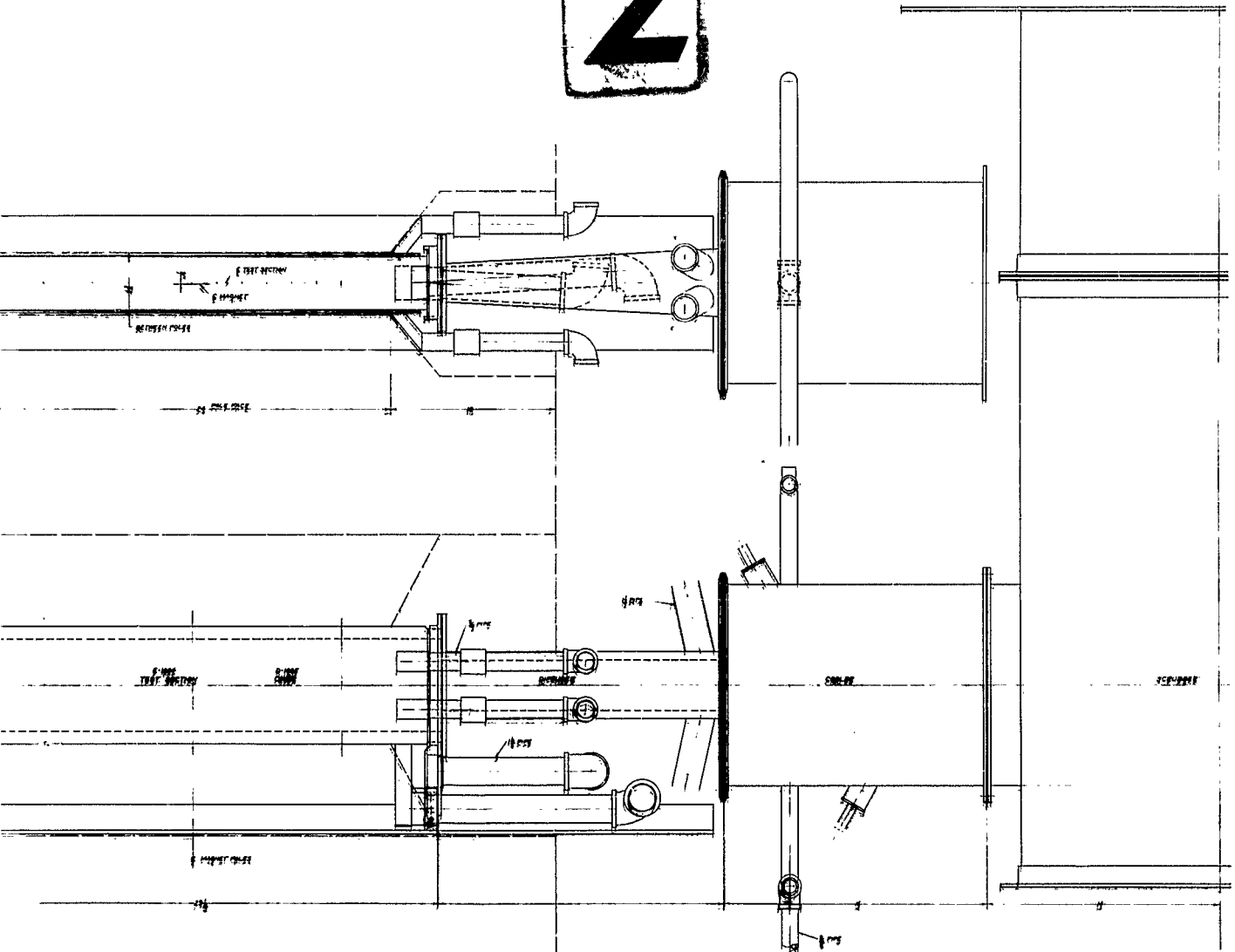
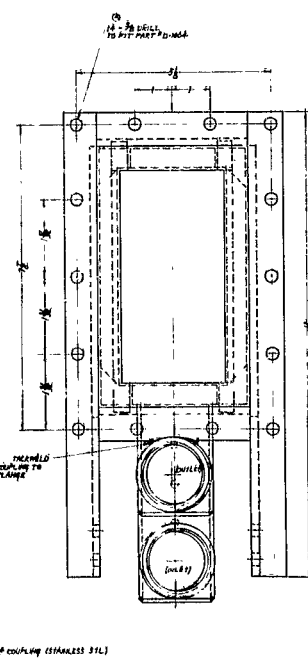


Figure 1
MGD Generator Assembly



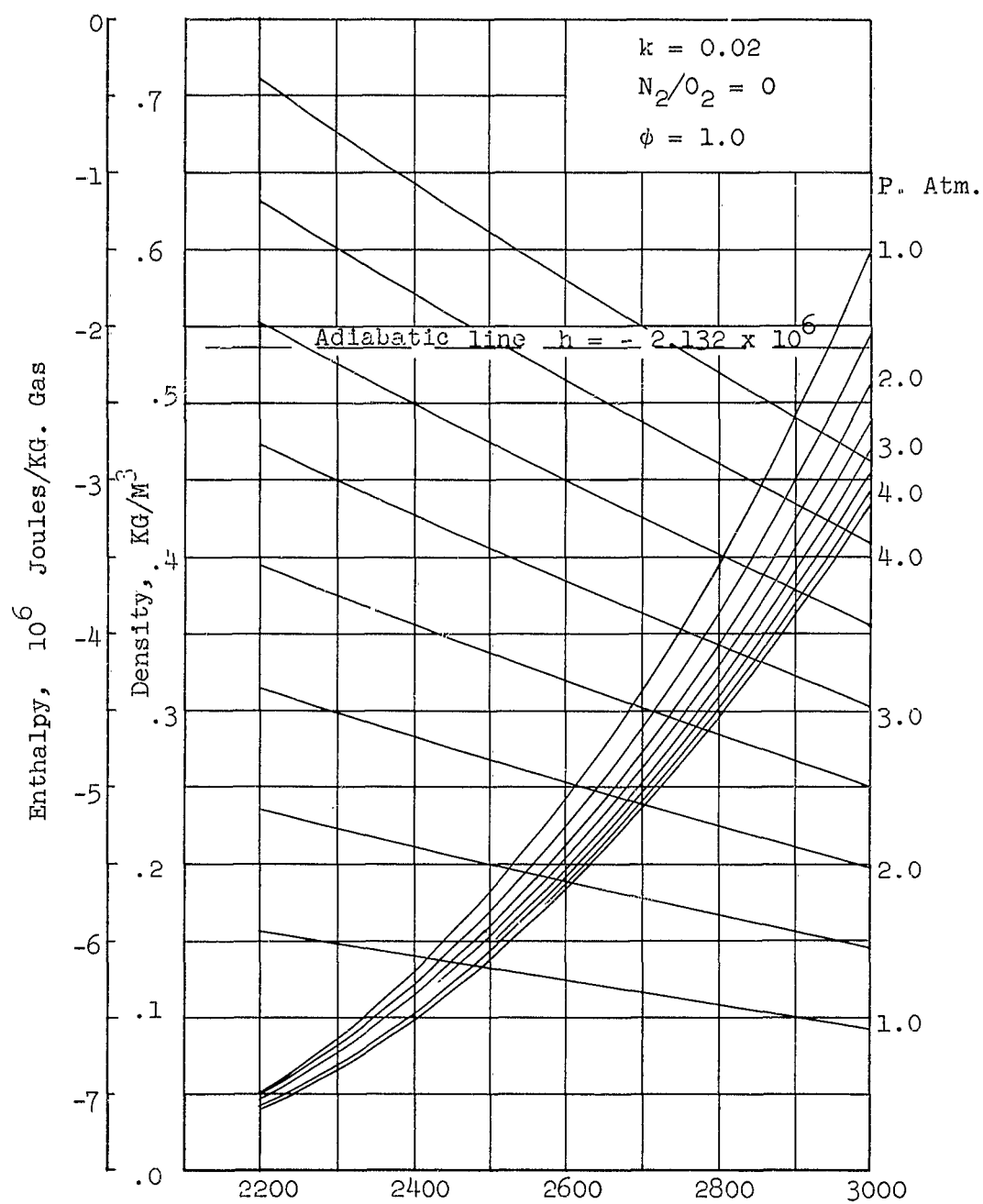


Figure 3

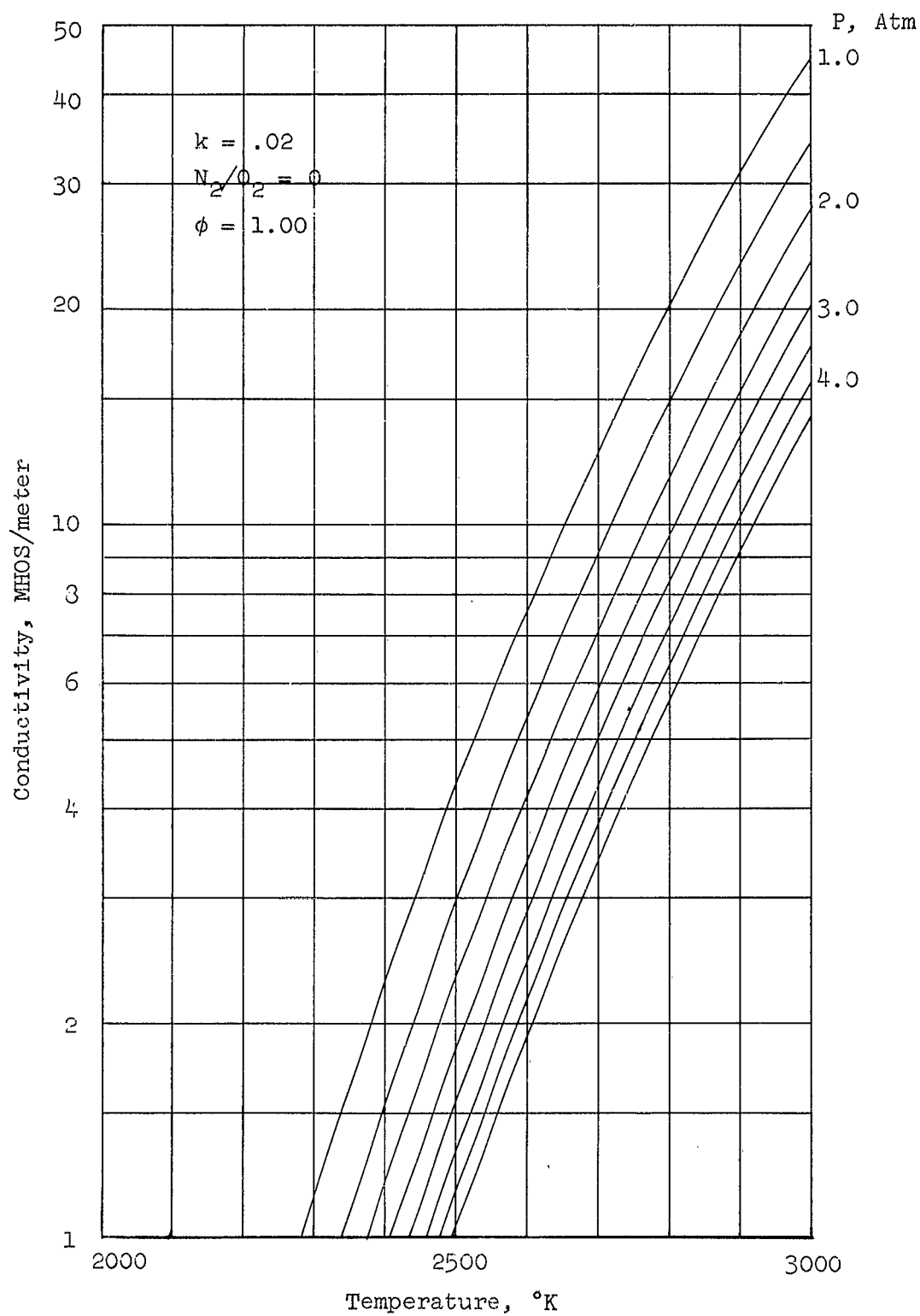


Figure 4

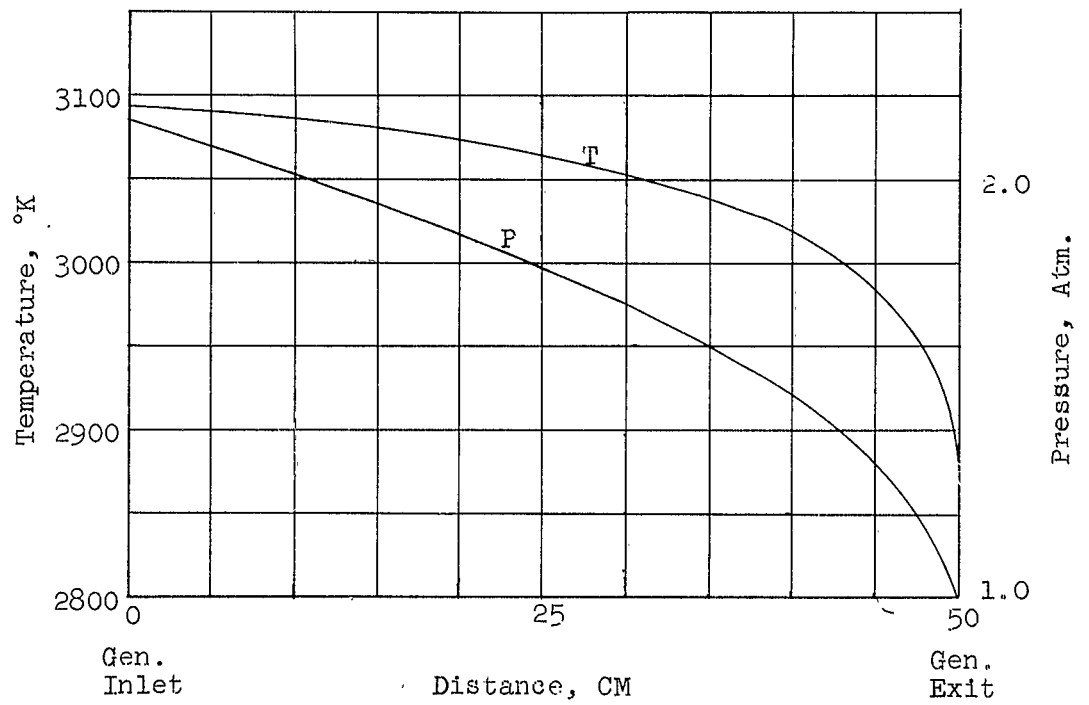
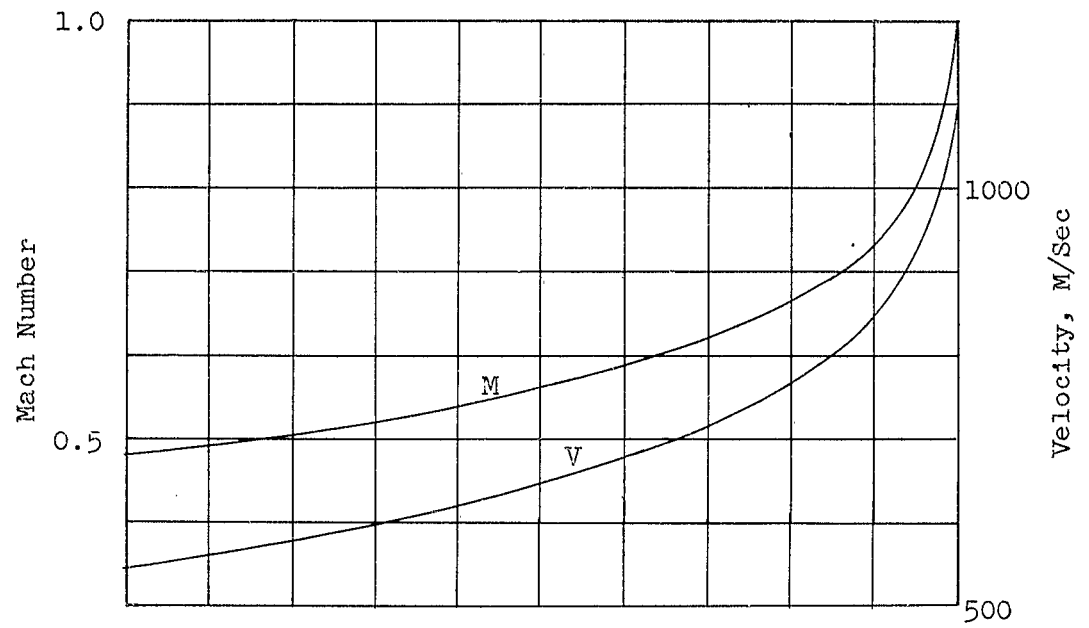


Figure 5

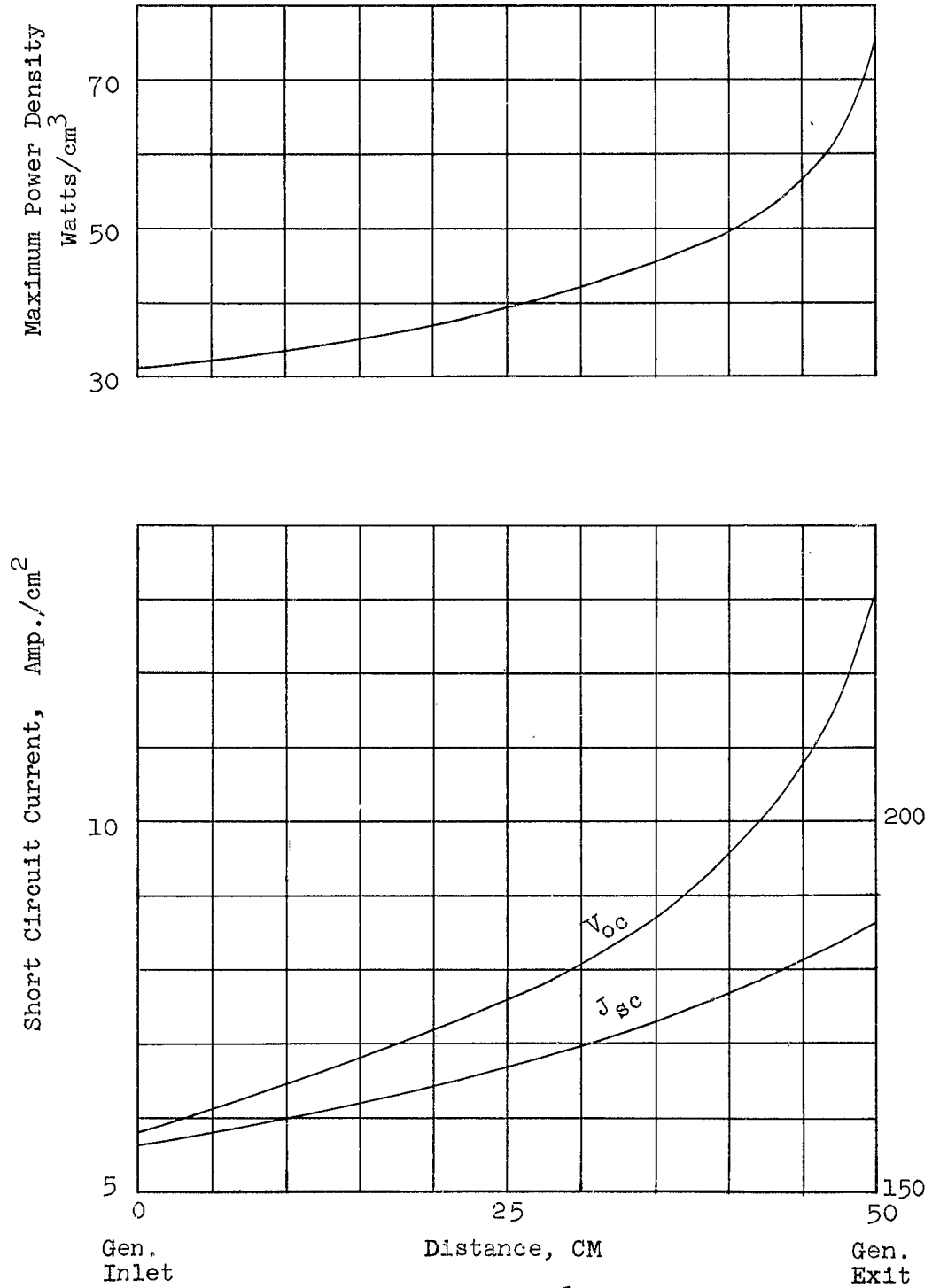


Figure 6
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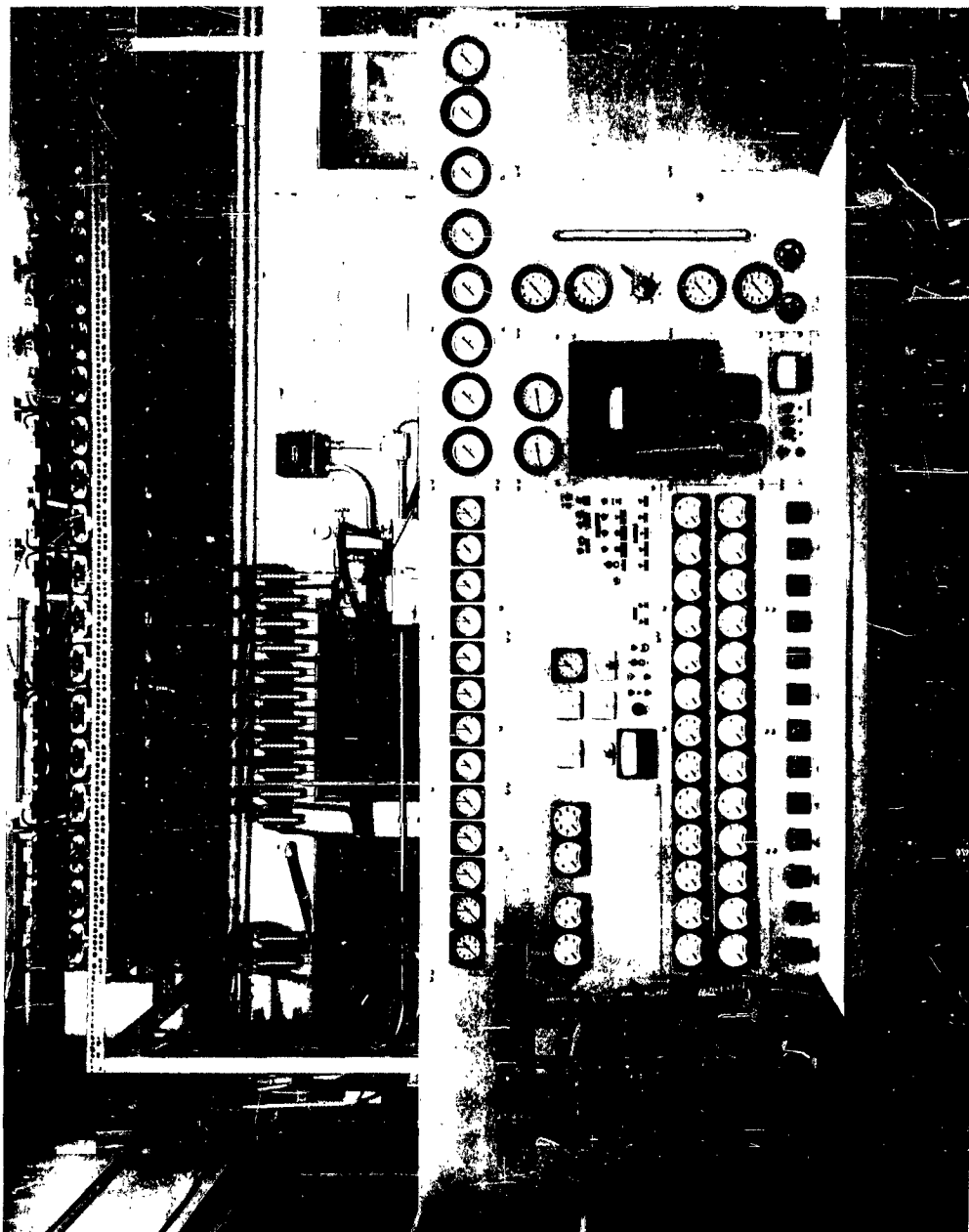


Figure 7
Instrument and Control Panel

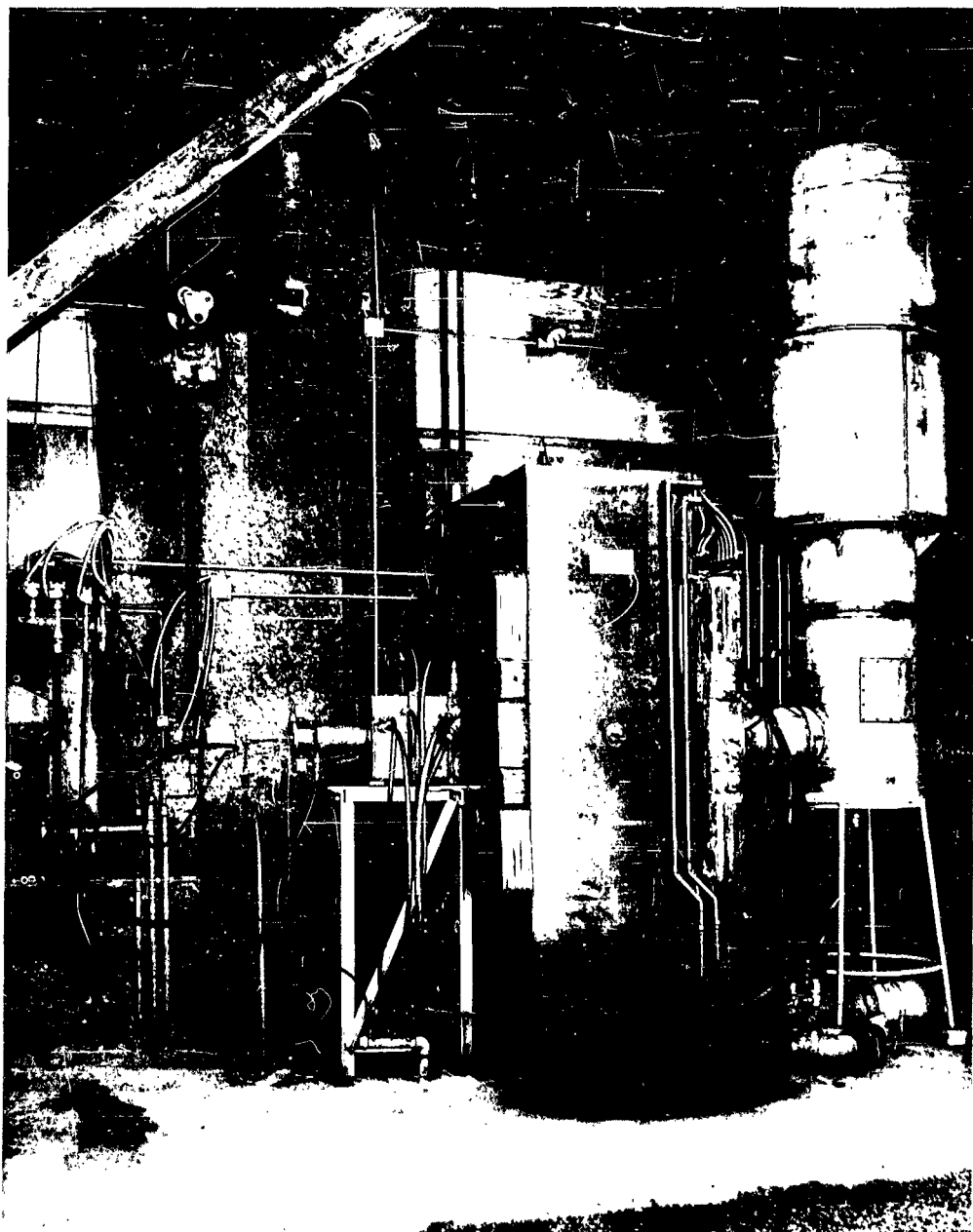


Figure 8
MGD Channel Assembled In Magnet

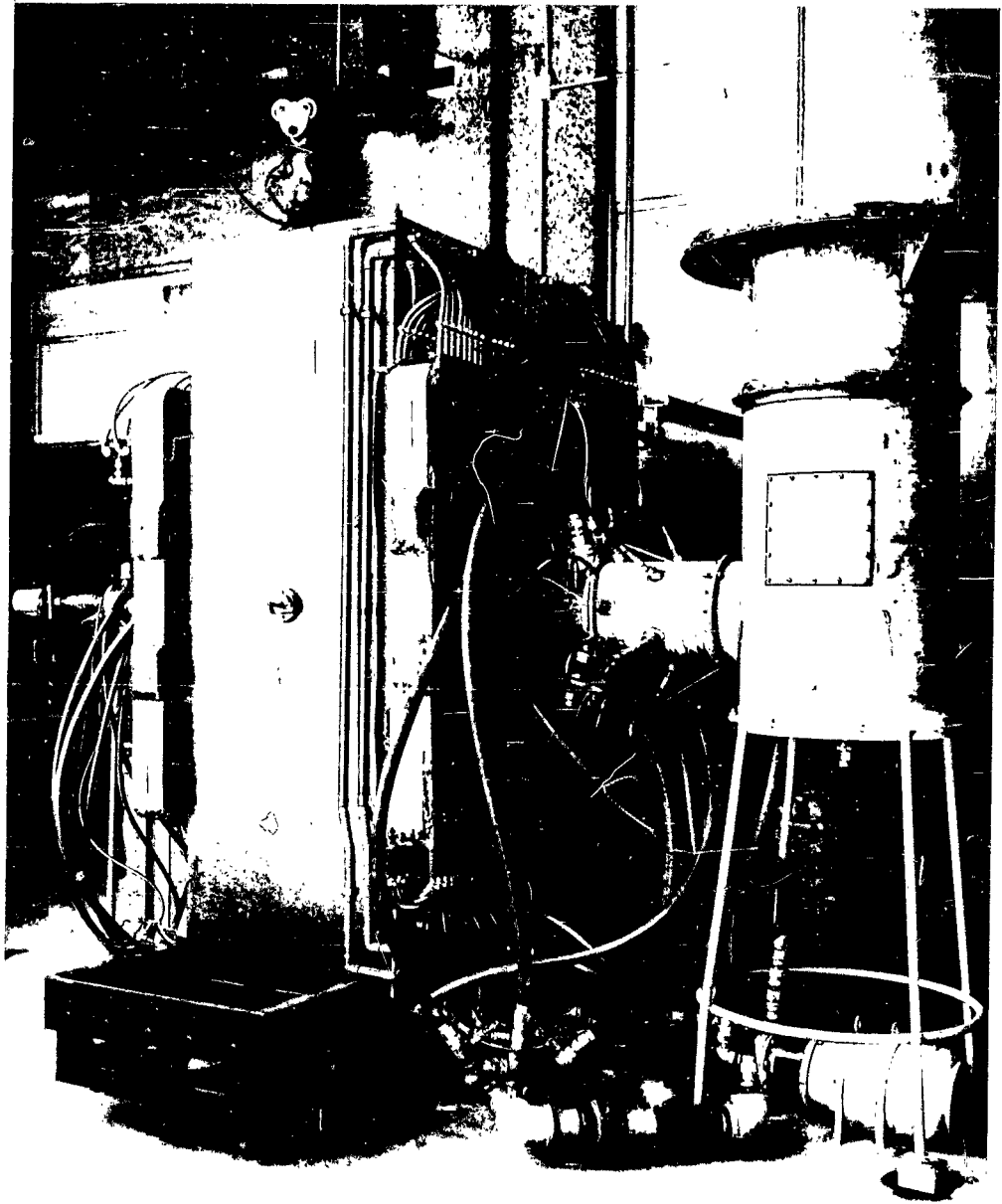


Figure 9
MGD Channel Assembled In Magnet

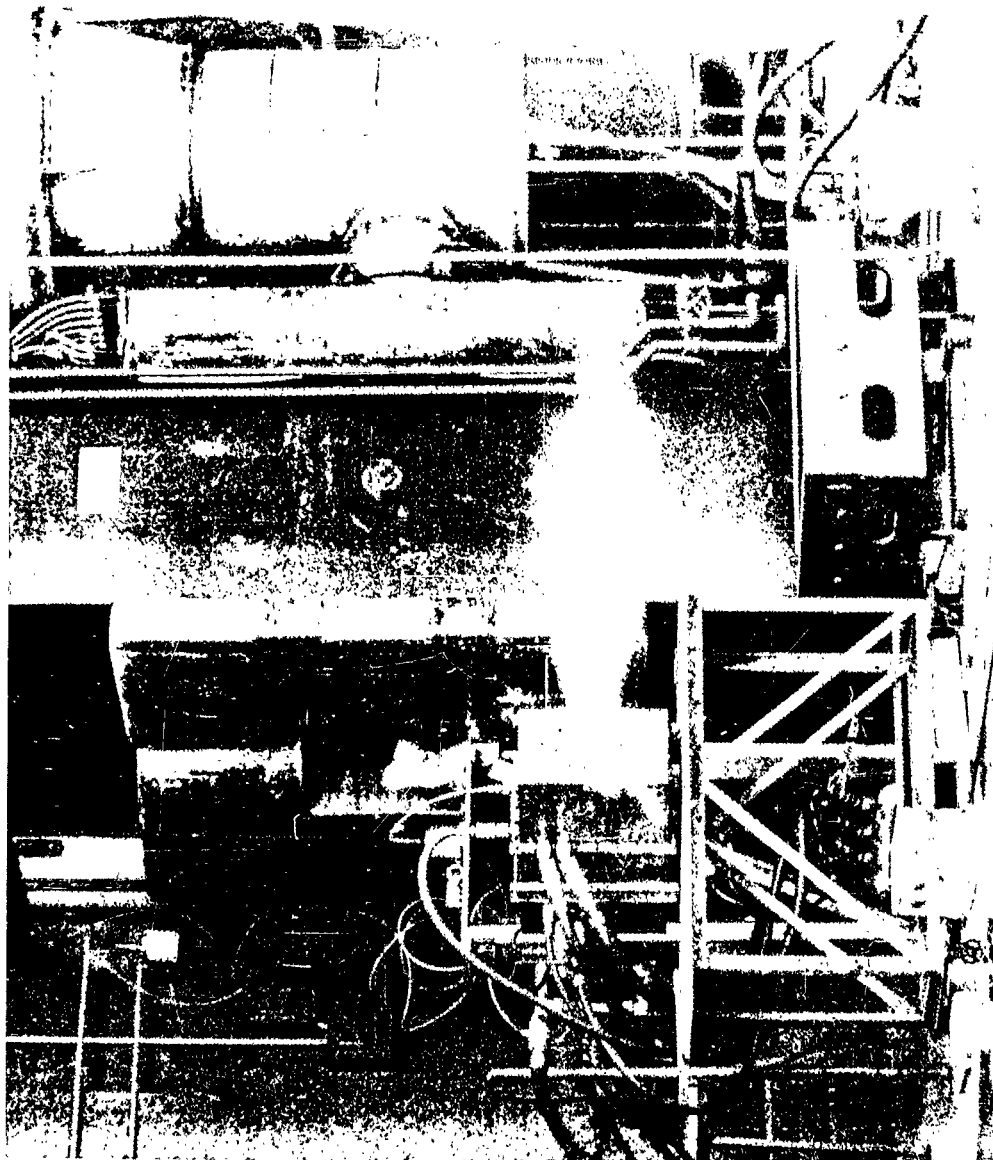


Figure 10
Burner Mixing Chamber Test
Section

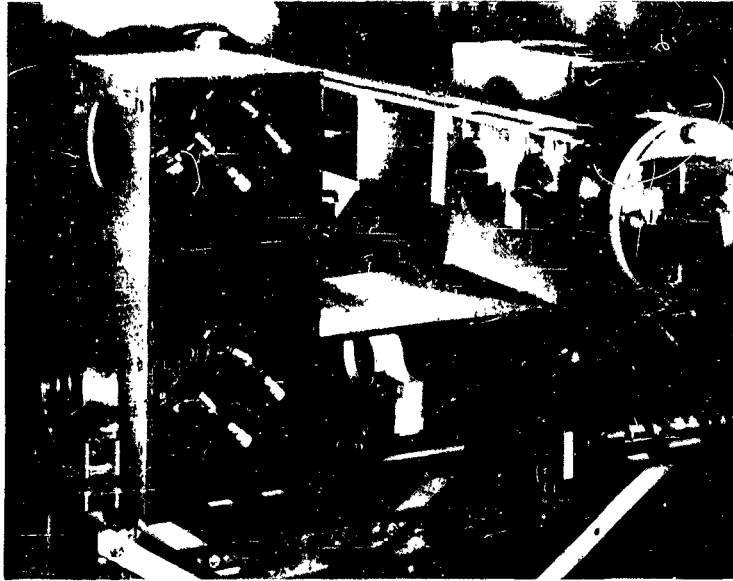


Figure 11 Interferometer

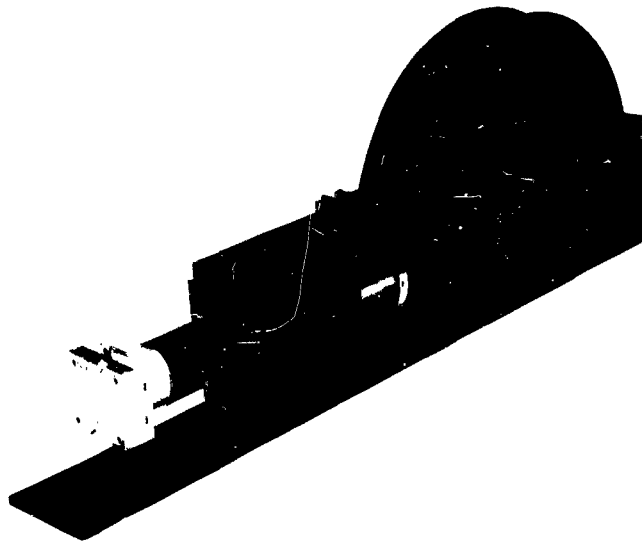


Figure 12 Rotating Mirror Camera

FRINGE SHIFT VS. MACH NO. & ELECTRON DENSITY

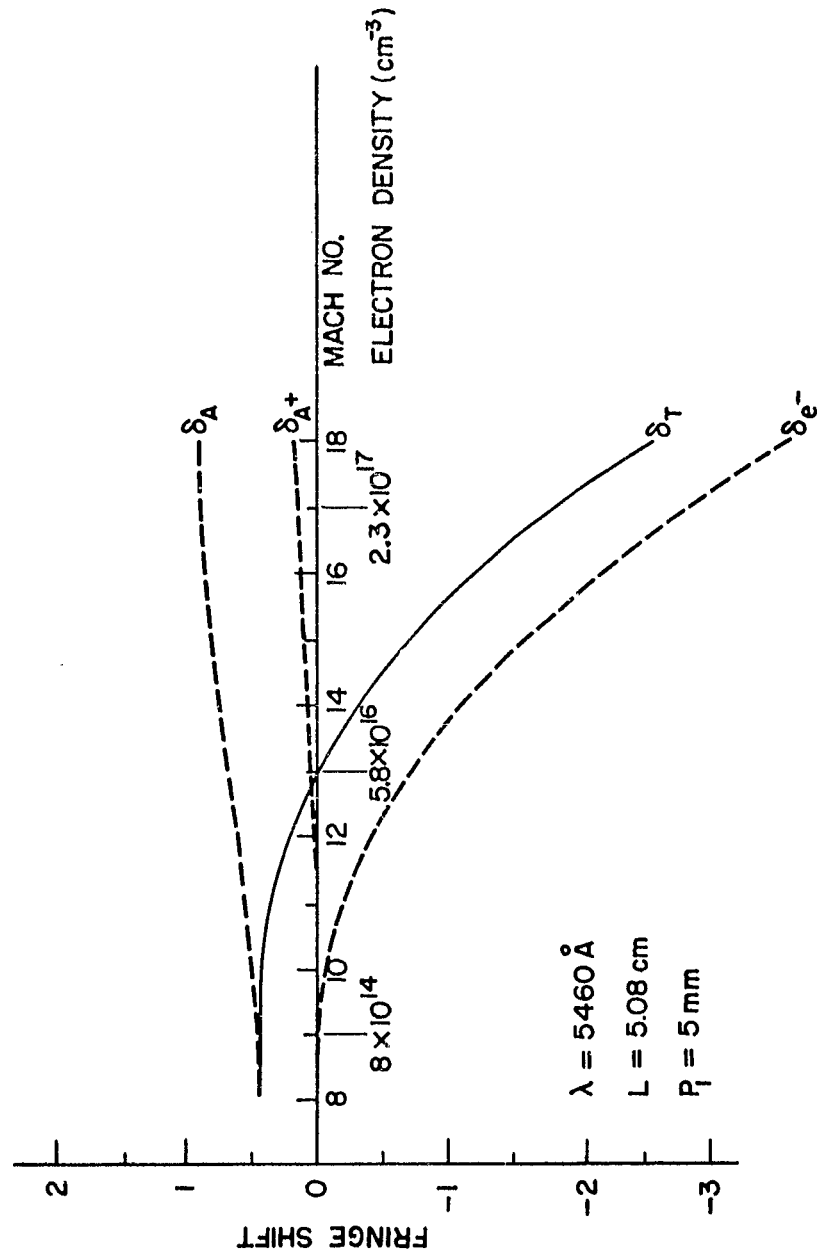


Figure 13

II. ELECTROCHEMICAL CONVERSION

The experimental and analytical work being carried out has as its main objective a better understanding of the mechanism of electrode catalysis particularly in the case of oxidation of hydrogen or hydrocarbon fuels. The investigations are continuing to be carried out on several fronts with emphasis on the role of the solid-electrode catalyst in the electrode process. Another part of the program is to examine carefully the combined catalytic and diffusional processes occurring inside a small cylindrical electrode simulating the behavior in a single pore of a multiporous electrode.

(1) Chemisorption Studies

The nature of the initial interaction of gaseous fuels with various transition element metals during the adsorption process in a non-electrolyte environment is being studied by measuring as a function of time the electrical resistance of a thin metal film. The resistance measurement can be used to establish the heat of adsorption which should indicate the type of chemical bonding for various fuel-catalyst combinations. It is hoped that these measurements will shed light on the nature of hydrocarbon chemisorption, an important step in electrode catalysis.

Work during the past six months has continued on the effect of adsorbed gas films on the resistance of thin metal films. During the past two months the work has been carried out on a reduced scale, since the research assistant assigned to the project has left Stanford and a replacement has not yet been made.

Much of the work in recent months has been focussed on the properties of thin silver films, one reason for this being that silver is an excellent non-electrochemical catalyst for the oxidation of olefinic hydrocarbons. The measurements involved have been similar to those reported earlier; i.e. we have evaporated thin films of silver, measured their resistance in vacuo and then examined the

effect of a gaseous atmosphere on the resistance. We have confirmed in some detail the preliminary results reported earlier, that the effect of adsorbed oxygen depends on the thickness (or, more accurately, the resistance) of the silver film. For very thin films of high resistance the effect of the adsorbed film at 25°C is to produce a decrease in film resistance. This effect may tentatively be identified as the adsorption of the ion O_2^+ or O_2^{++} on the surface, accompanied by the injection of electrons into the conduction band of the film. The effect of adsorbed oxygen at -195°C on such very thin films is in most cases negligible. For thicker films, e.g. those approaching several thousand Angstrom units and having, in our apparatus, resistances of about two thousand ohms, the effect of adsorbed oxygen is an increase in resistance similar to that observed with other metals such as nickel, though smaller in magnitude. Pure ethylene also appears to produce a decrease in resistance in silver films, and this effect is rather more difficult to account for. It seems a little unlikely that the ethylene is adsorbed as a positive ion--though the possibility cannot be ruled out -- and it may be that some dissociation of ethylene into either acetylene or an adsorbed acetylinic radical occurs, accompanied by the adsorption of hydrogen, probably in the form of protons.

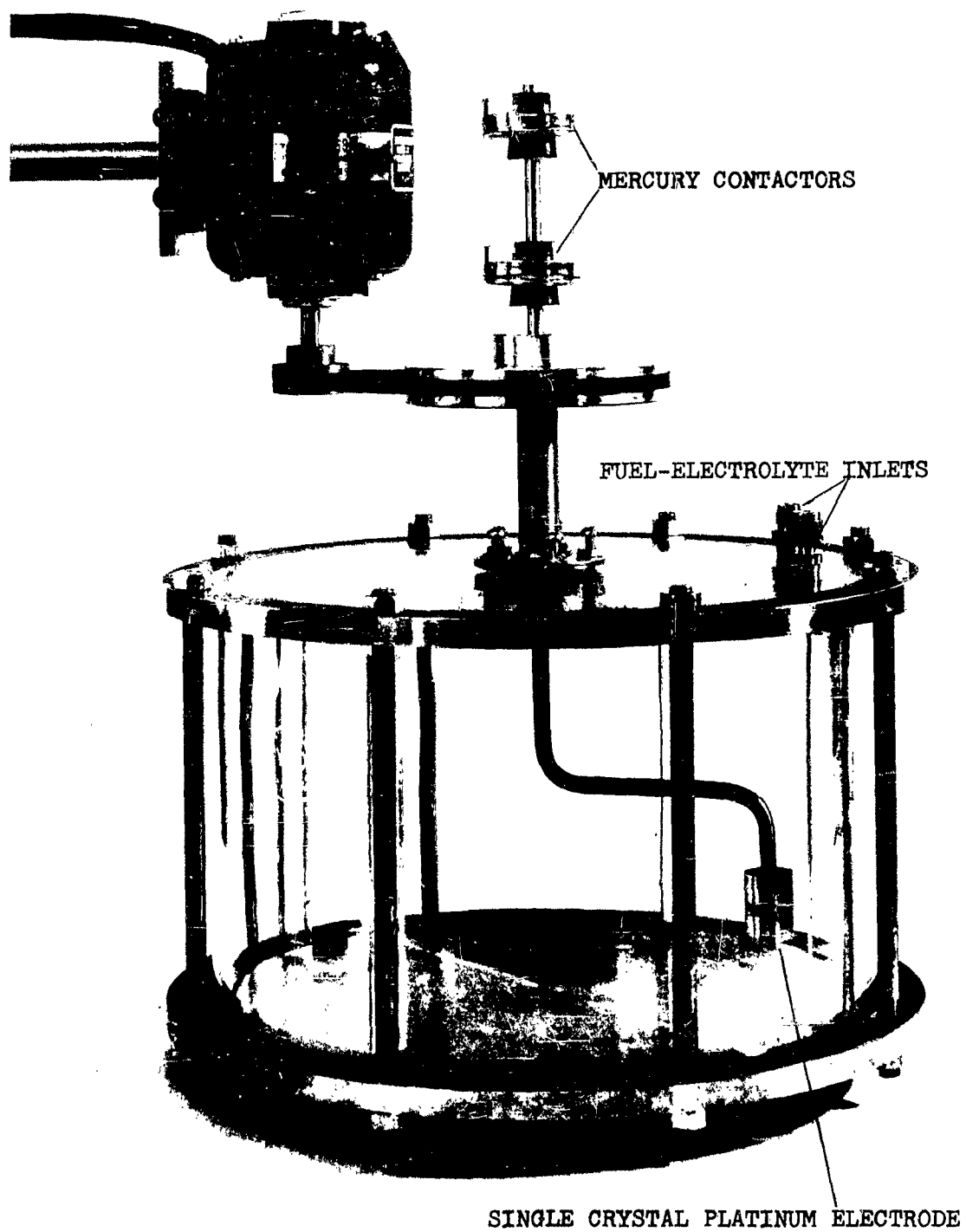
We have now, we believe, fairly well demonstrated that in physical and electrical properties it is possible to discriminate between the very thin films of silver which have properties that can be loosely classified as resembling those of a semiconductor, to the extent that they are quite atypical of bulk metal, and thick films whose properties are close to those of bulk metal. We now propose to investigate whether the change in physical properties is accompanied by a change in catalytic power. The reactions that we propose to investigate are (1) the

hydrogenation of ethylene and (2) the oxidation of ethylene, particularly paying attention to the character of this reaction in the presence of large excesses of such products as water and carbon dioxide.

(2) Study of Electrode Catalysis with Translating Crystal Electrode

In these studies small (approximately 1" long, 1/16" diameter) pure single crystal electrodes of transition elements which can be controllably doped with other elements are being used to study oxidation of hydrocarbon fuels. The electrolyte containing fuel flows normal at a desired velocity relative to the crystal. As will be described in more detail subsequently, flow of electrolyte fuel normal to the crystal is most conveniently accomplished in a closed-system (avoiding pumps) by having the crystal translate on the end of an arm which is rotating within the electrolyte bath. (See Figure 1). This fluid mechanical arrangement where the electrode is in the stagnation zone of a blunt body is quite different from the rotating disc or cylinder where rotation is about a central axis of the electrode. The steady state moving electrode is a valuable tool for studying electrode kinetics since diffusion resistance can be minimized and a constant, easily calculable concentration of uniformly accessible reactant fuel is continually exposed to the electrode surface. This device provides a convenient method of elucidating overall kinetic behavior since the reaction rate, obtained from a current measurement at a given voltage and velocity, and the fuel concentration accessible at the surface are both determined. This geometry has some advantages over other moving devices such as the rotating disc or cylinder in that the single crystal is in the stagnation region of a larger cylinder with fluid flow normal to the axis of the cylinder. In this simple fluid

FIGURE 1
FUEL CELL KINETICS



mechanical case a boundary layer thickness of constant value (and thus also the surface concentration of reactant) over the whole crystal is obtained which can easily be varied by varying the velocity of the crystal. The rotating disc is subject to edge effects not present in this geometry. Also in the case of the translating electrode a small single pure crystal of needle or cylindrical shape may be employed permitting solid-state conditions and doping to be carefully controlled. A disc-shaped pure crystal of many elements would be difficult to grow. The importance of such factors as the particular crystal face exposed and dislocation population will be established by physical technique such as x-ray microscopy and chemical etching techniques. In development of the translating platinum electrode hydrogen has been used as the fuel because of the mass of kinetic data available for this fuel. Other studies are being made on the kinetics of oxidation steps of methanol, a more practical fuel.

(a) Development of Translating Crystal Electrodes for Catalysis Studies

During the past six months theoretical and experimental efforts have been directed toward the development of the translating electrode device as a means of studying diffusion and kinetics of electrochemical processes. The work can be divided into the following categories:

- 1) Theoretical analysis.
- 2) Experimental verification of theory
- 3) Use of the translating electrode device for electrochemical kinetics with single crystals.

An analysis of the hydrodynamical flow was facilitated by means of boundary layer theory which enabled the determination of the thickness of the laminar boundary layer as a function of the rotational speed. The following expression was obtained:

$$\delta = 3.7 \left(\frac{v d}{\Omega R_s} \right)^{1/2} \text{ cm} \quad (1)$$

where v = kinematic viscosity of solution
 d = diameter of cylinder in which the electrode is imbedded
 R_s = radius of rotating shaft
 Ω = angular velocity in revolutions per minute (RPM)

By combining the boundary layer equations with the diffusion equation, the thickness of the diffusion layer, δ_x , can be determined.

The current density is proportional to the concentration gradient of the diffusing species evaluated at the solid-liquid boundary and can therefore be obtained from the solution of the diffusion equation. The resulting expression for the current density is:

$$I = 1.52 \frac{n F D_{i,m}}{d} (N_{Sc})^{1/3} (N_{Re})^{1/2} (C_{i\infty} - C_{is}) \quad (2)$$

where n and F have their usual significance and

$D_{i,m}$ = multicomponent diffusion coefficient of species i

N_{Sc} = Schmidt number $\frac{v}{D_{i,m}}$

N_{Re} = Reynolds number $\frac{\pi R_s \Omega d}{30 v}$

$C_{i\infty}$ = concentration of i in the bulk electrolyte

C_{is} = concentration of i at the solid surface.

It can be seen from equation (2) that the concentration of the diffusing (i.e. reacting) species at the electrode surface can be easily calculated from experimental measurements of current density. If we consider the case of the oxidation of hydrogen in acid electrolyte the following simple expression is obtained from equation (2) for a typical geometry used in these studies:

$$C_{H_2,s} = C_{H_2,\infty} - (2)(10^{-3}) I/ \quad (3)$$

For reactions which are not controlled by diffusion, equation (2) can be used to determine the dependency of the reaction rate on the surface concentration.

Under conditions of total diffusion control, equation (2) with $C_{1s} = 0$ gives the limiting current density. For the H_2 oxidation in acid the limiting current density can be obtained from (3) (again setting $C_{H_2,s} = 0$). Thus

$$I_{Lim} = 0.382 \sqrt{\Omega} \text{ ma/cm}^2 \quad (4)$$

In order to test the translating electrode device an electrochemical system was needed for which there would be ample experimental data in the literature. Several systems were tried such as H_2 reaction on platinum, copper dissolution in sulfate solution, and mercury dissolution. In the latter case the mercury electrode was made by amalgamating a small platinum cylinder so there is some question as to whether this is a true mercury electrode or a combination of mercury and platinum. The copper system was very sensitive to traces of O_2 and the results were inconclusive. The H_2 reaction on platinum was tried in N KOH solution using the Hg/Hg O reference and in acid solution (N H_2SO_4) using the Hg/Hg $_2$ SO $_4$ reference. In these latter systems the rest potential varied appreciably with rotational speed and it was felt that the close proximity of the reference electrodes to the Pt working electrode caused spurious potentials due to the presence of Hg and Hg $_2^{++}$ ions. In view of these difficulties it was decided to use an H_2 reference electrode and consider the H_2 reaction on platinum in acid medium.

Current-voltage measurements were first carried out on a smooth polycrystalline platinum electrode. Some of these curves are shown in Figure 2. It can be seen that for potentials below about 300 mv the current plateau is

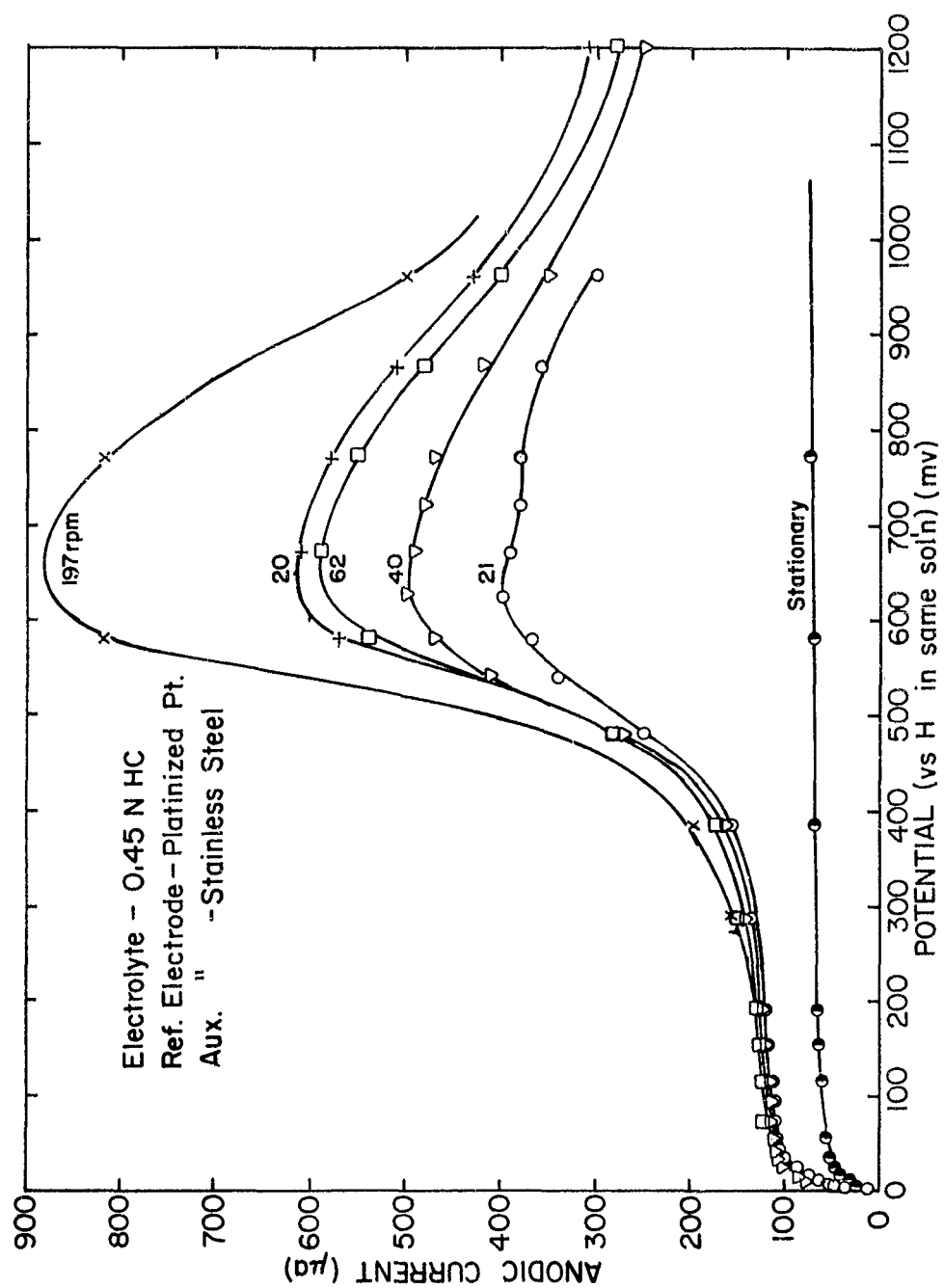


FIG.2 Polarization Curves for Translating Bright Polycrystalline Platinum Electrode.

independent of the translational speed and therefore unaffected by changes in the diffusion layer thickness. This behavior is suggestive of a kinetically controlled process which might arise because of a saturation of active sites on the catalyst surface. In the vicinity of 0.65 volts the current reaches a peak value which varies linearly with the square root of the rotational speed. Attempts are being made to analyze this rather curious behavior.

The electrode used to obtain the curves in Figure 2 was then platinized and a series of polarization curves obtained for the platinized electrode. These curves are shown in Figure 3. Here the current reaches a maximum at about 100 mv and remains essentially independent of the applied potential up to the oxygen evolution potential. No peaking at 0.65 volts was observed. The dependency of the limiting current on the square root of Ω (RPM) is linear as predicted by the boundary layer analysis. The fact that theory indicates a non-zero concentration of H_2 at the electrode in the limiting-current case has led to the decision to make more measurements to explain this interesting observation.

A cylindrically shaped single pure crystal platinum electrode 2 mm in diameter by 1.5 cm long was imbedded in the leading edge of a 1.91 cm diameter lucite cylinder in the same manner as the polycrystalline platinum. Cleaning and preparation of the electrode involved only two hour immersion in strong KOH to remove grease followed by distilled water rinsing and cathodizing for 1-1/2 hours at 40 ma. A series of anodic polarizations was carried out using a potential sweep of 33 mv per second with the electrode stationary. The sweeps were from 0-1 volt and after 3 sweeps were quite reproducible. The null potential, however, did not go to zero indicating that there may have been impurities present on the crystal surface. This was observed with the polycrystalline electrode in some preliminary

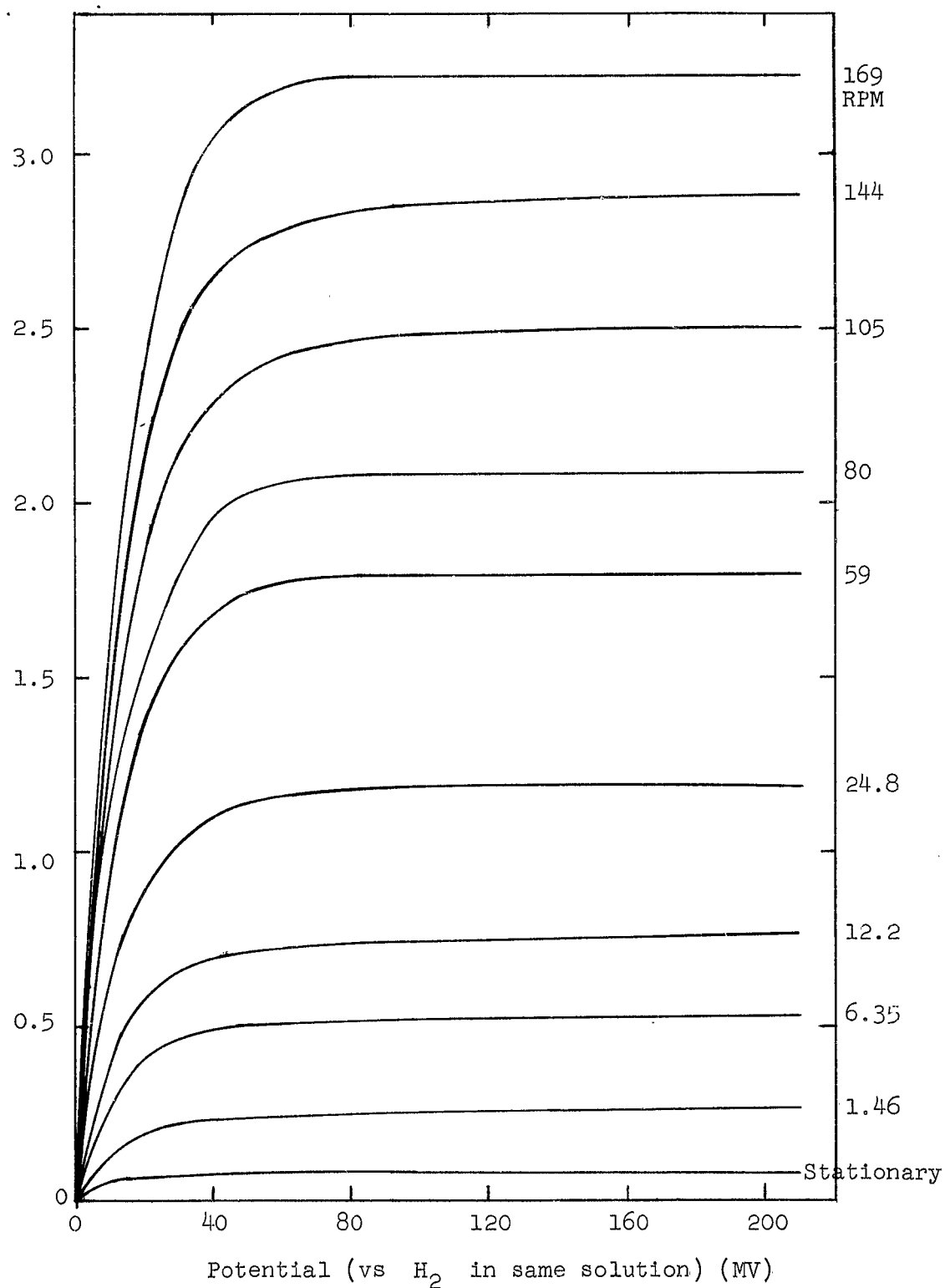


Figure 3 - Polarization Curves for Translating Polycrystalline Platinized-Platinum Electrode

measurements and was overcome by treating the electrode with dilute aqua regia. Nevertheless these preliminary tests with the single crystal platinum electrode appear to indicate a behavior similar to the polycrystalline electrode with a rapid rise in current at about 300 mv and a peak current at 0.65 volts.

The single crystal electrode will be re-cleaned to obtain an active surface and further tests will then be conducted to obtain quantitative results. An evaluation of the data obtained for the various electrodes is being made and it is hoped that a satisfactory explanation of the results will be achieved in the near future.

(b) Influence on Electrode Catalysis of Dislocations and Dopants in a Single-Crystal Platinum Electrode
-- Methanol Oxidation

The object of this work is the investigation of the effect of surface condition upon the efficacy of an electrode in promoting a reaction of ultimate interest to fuel cell applications. Although most electrodes in practical use are solids, generally metals or carbon, a disproportionate amount of basic experimental electrochemistry has been done with the mercury electrode because of the extreme difficulty of obtaining and keeping a reproducible solid surface. In recent years, understanding of the solid state has advanced considerably⁽¹⁾ and has led to attempts to relate catalytic activity of a surface to more fundamental properties⁽²⁾. Since an electrochemical reaction can be regarded as an electron-transfer process catalyzed by the electrode surface, perhaps consideration of the relationship between the catalytic properties of the electrode surface and certain solid state quantities could lead to the design of materials with desirable electrochemical action.

(1) Gray, T.J. et al. "The Defect Solid State", Interscience, N.Y. 1957, (Cf. particularly pp. 239-292).

(2) Schwab, G.M., J. Chem. Phys. 51 (1954).

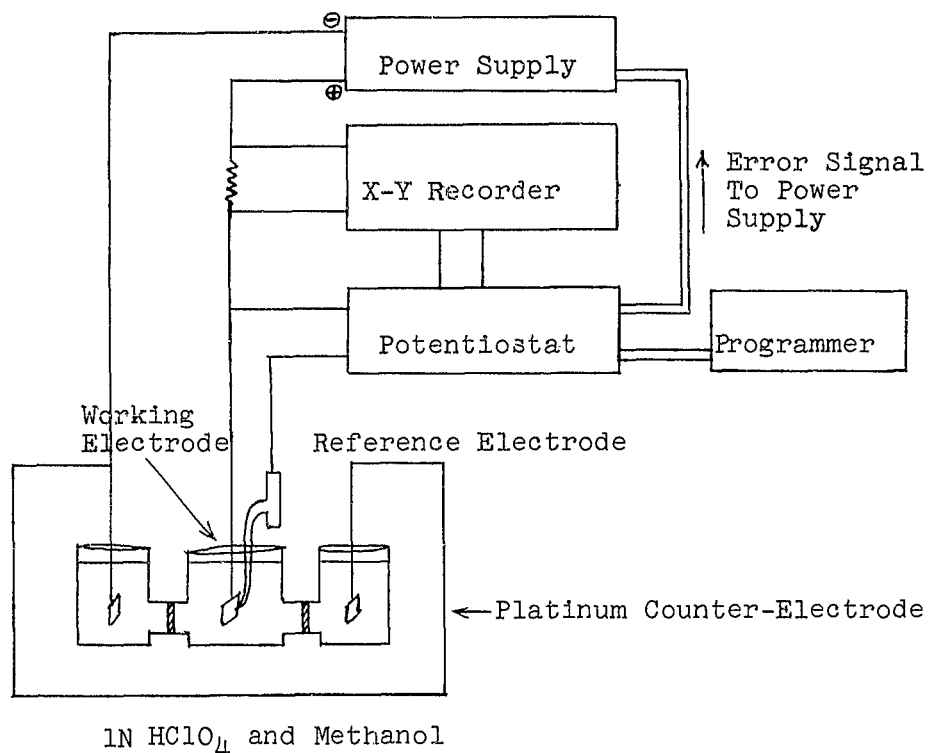
In particular, an investigation of the effect of surface dislocations and doping of an electrode upon its electrochemical activity for anodic oxidation of a fuel might yield basic information of value to the fuel cell field. The electrode material and electrolyte in such a study could well be chosen to give relatively wide applicability of any results of the work and also for ease in conducting the electrochemical and solid-state experiments. Of the many electrochemical systems that satisfy these two criteria, we have chosen single crystal platinum as the electrode and an acidic aqueous solution of methanol as the fuel.

Work during the past year accomplished two things: i) the objective was defined more specifically and the method of attack was formulated, and ii) the experimental apparatus was constructed. The specific object of this work is to investigate the influence of surface dislocations and doping on the electrode activity of platinum single crystal in the anodic oxidation of methanol in acid solution. Methanol was chosen since it is the simplest hydrocarbon derivative that is completely miscible with water, and it is felt that such a study should precede further investigation with rather insoluble systems, e.g., CH_4 , C_2H_4 , etc. Since formaldehyde and formic acid are intermediates in the anodic oxidation of methanol to carbon dioxide and water⁽³⁾, some studies of anodic behavior of these materials will also be undertaken. The supporting electrolyte in all cases is 1N HClO_4 since this material is fully ionized, adsorbed very weakly, and it does not tend to form complexes.

The apparatus, shown schematically below, is suitable

(3) Buck, R.P., L.R. Griffith, R.T. Macdonald and M.J. Schlatter, California Research Corporation, "Investigative Study Related to Fuel Cells", Progress Reports 1 - 4 (1960-61) DA-49-186-502-ORD-929.

for qualitative studies of catalytic activities. It is planned to extend the scope of the investigation of these systems by studies with the translating electrode.



The cell is made of pyrex glass, the fine sintered glass discs being used to minimize catholyte-anolyte mixing; ground glass covers minimize contamination from the atmosphere. In addition, it has a small glass stirrer and provision for bubbling purified argon through the electrolyte to remove dissolved oxygen. The argon supplied to the cell is "prepurified" tank grade which has been passed over hot copper gauze in a quartz tube, ascarite, molecular sieves at dry ice temperature, and water in order to remove the last traces of impurities and to saturate the argon with water vapor to prevent excessive evaporation of cell

electrolyte. The reference electrode is a saturated calomel half-cell with a 1N HClO_4 salt bridge containing a fine sintered glass disc to minimize diffusion.

The circuit is designed to permit the potential of the working electrode (i.e., the single crystal) to be held at a predetermined value with reference to the calomel electrode by automatic regulation of the anode current density. By systematically varying the potentiostat setting, a plot of anode current versus potential can be made with the X-Y recorder. Provided that the solution is stirred sufficiently, the current plotted in this way will be limited by a catalytic activation step at the electrode surface. The extent of catalytic activity of the anode for the slow step in the electrochemical oxidation of the fuel can thus be measured. Although other workers^(3,4,5,6) have studied the mechanism of methanol oxidation on precious metal anodes, as far as we know no attempt has been made to relate electrocatalytic activity for this reaction to specific measurable surface properties of a single crystal electrode.

Preliminary runs with this apparatus on the methanol system on polycrystalline platinum are in agreement with Gilman and Breiter⁽⁴⁾ at their slower sweep rates. Our programmer does not now permit sweeping at rates higher than 0.4 volt per second but higher rates would require only minor modification of the equipment. The reproducibility of runs and the reliability of the system are judged to be sufficiently good that the apparatus is now being used routinely.

(4) Gilman, S., Breiter, M. W., General Electric Research Laboratory, Report No. 62-RL-(2949 C/M).

(5) Mueller, E., S. Tanaka, Z. Electrochem. 34, 256 (1958).

(6) Tafel, Z. Phys. Chem, 1905, 50A, 641.

To date, no platinum single crystals have been used in this work, but rather polycrystalline platinum rod of the same geometry as the single crystals to be used later has been subjected to the same solid-state and electrochemical treatment in order to develop our technique and also to give a basis for comparison of the anticipated single crystal data. Doping and dislocation counting are being done under the direction of Professor D. A. Stevenson of the Materials Science Department. The doping procedure consists of cleaning the platinum electrode ($1/8$ inch diameter by $5/8$ inch long with 0.025 inch platinum wire spot welded to one end) in KOH and in aqua regia, sealing it and the dopant under vacuum in a quartz ampule, and diffusing in a high temperature furnace. The time and temperature of each diffusion run will be determined from an estimate of the diffusion rate and solubility of each dopant. Dislocation density will be measured by chemical etching and etch-pit counting under a light microscope.

The activity of the anode depends upon the presence or absence of platinum oxides and hydroxides and upon species adsorbed on the electrode surface as well as on dislocations and doping. Considerable literature exists on the formation and dissolution of platinum-oxygen compounds on electrodes immersed in aqueous solutions^(7,8,9), and considerations of chemical composition of the electrode surface such as are discussed there will be of the utmost importance in interpreting our polarization curves. Therefore, in addition to characterizing the surface of the metal crystal before a run, it will be necessary to look for evidence of electrochemically induced changes during the course of the potential sweep in the electrolyte.

(7) Hoar, T.P., Proc. Roy. Soc. (London) A, 1933, 142, 628.

(8) Randles, J.E.B., Diss. Farad. Soc., 1947, 1, 11.

(9) Ershler, B., Diss. Farad. Soc., 1947, 1, 269.

In summary, it is proposed to continue the work now in progress to attempt to relate the anodic activity for methanol oxidation of a platinum single crystal to its surface dislocation density and dopant concentration.

(3) Electrode Catalysis by Faradaic Impedance Method

Instrumentation for the Faradaic Impedance technique for measuring reaction and adsorption kinetics has been set up. It is felt with the independent techniques of sections 1, 2, 3, that the kinetic behavior of fuels with selected electrodes may be elucidated.

In all electrochemical reactions there exist several factors affecting the rate of the process. For an ion reaction without deposition or dissolution of metal at the electrode surface, it may be postulated that the reaction sequence will be:

1. Diffusion of the reacting ion to the electrode surface.
2. Adsorption of the reacting ion on the electrode surface.
3. Electron transfer from the electrode to ion (or vice versa).
4. Desorption of product of reaction.
5. Diffusion away from the electrode surface by the products of the reaction.

It may be assumed that this sequence would be general for most anodic and cathodic reactions and that the rates of diffusion of most reactants and products of electrochemical reactions would be of the same order of magnitude for a given electrolyte. Therefore the major factors differentiating the overall speed of different electrochemical reactions would be the sequence 2 to 4 and particularly the electron transfer step. Irreversible to slow reactions may be characterized by plotting the Tafel⁽¹⁰⁾ relation

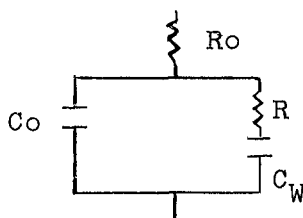
$$E - E_0 = \eta = a + b \ln i$$

(10) Tabel, Z. Phys. Chem, 1905, 50A, 641.

to obtain the exchange current i_o , the value of the current flowing at the reversible potential such that $i_a = i_c = i_o$ which was first suggested by Hoar⁽¹¹⁾. As the electron transfer steps become faster and thus the electrode reactions more reversible, the exchange currents involved assume magnitudes that are too great to be measured from conventional current -- voltage curves and thus so called relaxation techniques must be used. The methods by which relaxation techniques operate are such that when electrode systems are perturbed from their equilibrium potentials, the rates at which the systems react to neutralize the perturbations are analyzed.

One of the most useful relaxation techniques is that of the faradaic impedance at the electrode surface^(12,13). A small sinusoidal A C wave is passed through the electrode and the complex impedance is measured with an impedance bridge. Knowing the frequency of the signal (f) the ohmic resistance of the solution (R_o) and the capacity of the double layer (C_o) the admittance due to the electrode reaction (Faradaic Current)⁽¹⁴⁾ may be separated from the charging current.

Thus the impedance may be tentatively indicated as a network of capacities and resistors in series and in parallel.



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- (11) Hoar, T.P., Proc. Roy. Soc. (London) A, 1933, 142, 628.
 - (12) Randles, J.E.B., Diss. Farad. Soc. 1947, 1, 11.
 - (13) Ershler, B., Diss. Farad. Soc., 1947, 1, 269.
 - (14) Grahame, D.C., J.A.C.S., 1949, 71, 2975.

It has been shown⁽¹²⁾ that when an electrode reaction is extremely fast, total diffusion control is obtained and that $R = \frac{1}{\omega C_W}$ where $\omega = 2\pi f$. Any deviation from this condition may be accounted for by the rate of the electron transfer step, which appears as an additional resistance in R. Strongly adsorbed reactants or products may appear as additional impedances associated with the above electrical network⁽¹⁵⁾.

A complementary method to faradaic impedance technique is galvanostatic perturbation. In this method a constant current is passed through the electrode and the consequent change of potential with time recorded. Early work of Delahay and Mattax⁽¹⁶⁾ indicated the applicability of the method to irreversible reactions, whilst the later work of Delahay and Berzins⁽¹⁷⁾ showed the evaluation of rate constants for reversible reactions. Corrections for adsorption by reaction species in the galvanostatic technique are difficult and thus correlation of impedance measurements to galvanostatic measurements may be desired.

Previous work on the hydrogen electrode reaction was carried out by Ershler⁽¹⁸⁾ who indicated that adsorption at the electrode played a major part in the reaction on Platinum. Knorr⁽¹⁹⁾ et al. also carried out impedance measurements at Platinum electrodes. The results of Justi⁽²⁰⁾ et al. of the hydrogen reaction on Raney Nickel electrodes are confusing

(15) Randles, J.E.B., H.A. Laitinen, Trans. Farad Soc., 1955, 51, 54.

(16) Delahay, P., C.C. Mattax, J.A.C.S. 1954, 76, 874.

(17) Delahay, P., T. Berzins, J.A.C.S. 1955, 77, 6448.

(18) Ershler, B., P. Dolin, Acta Physiochim. USSR 1940, 13, 747.

(19) Breiter, M., H. Kammemaier, E.A. Knorr, Elekt. Chem. 1954, 58, 702.

(20) Justi, E., et al. "High Drain H₂ Electrodes". E 541 Pergamon.

and it is difficult to credit that reliable results could be obtained within the microscopic pores of a sintered electrode without consequent shielding.

Further work to clarify and extend the research on the mechanism of hydrogen electrode on Platinum, Palladium, Gold and Nickel is needed together with the rates of reaction for the oxidation of hydrazine and some carbonaceous fuels. The influence of a second metal on the electrode, forming an alloy, such as Lithium in Nickel used in the Bacon⁽²¹⁾ cell and Iridium in Platinum would be investigated.

Fuels being studied must be soluble in the electrolyte under consideration as the electrode mechanism can only take place via the liquid phase, be it only a thin meniscus film, the solubility of the fuel cannot, however, exceed that of a saturated solution. One might envisage a minimum practical solubility of 10^{-3} moles l^{-1} of fuel in electrolyte.

Upon considering the most suitable electrolyte-fuel-systems, one must bear in mind that the electrolyte must also be conducive to an oxygen electrode. It has been shown that the oxygen electrode is reversible in aqueous alkali and kinetic rate constants have been evaluated⁽²²⁾. In acid solutions on Platinum and Gold⁽²³⁾ the reaction is irreversible and pH dependent. In molten electrolytes, however, the oxygen electrode is reversible. By using high temperature molten electrolytes, the use of carbonaceous fuels is facilitated as carbon deposited at fuel electrodes may be removed at these higher temperatures.

It is suggested that measurements of electrode kinetics should be carried out in aqueous and molten electrolytes with various fuels and metal electrodes using faradaic impedance and galvanostatic techniques.

(21) Bacon, F.T., "Fuel Cells I", p. 51.

(22) Stonehart, P., Ph.D. Dissertation Cambridge, 1962.

(23) Bockris, J. O'M., L.F. Oldfield, Trans Farad Soc. 1955, 51, 249.

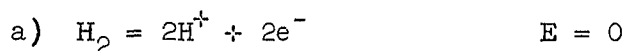
Experimental

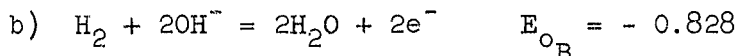
To measure the complex impedance at a fuel electrode a Wien bridge has been built using decade resistance boxes for ratio arms and a series combination of a decade capacitance box and decade resistance box for a balancing impedance. The applied signal can be varied from 20 cps to 10 kcs with a maximum of 1% error in impedance measurement, the amplitude of the A.C. signal being of the order of 5mv. The bridge and cell arrangement are essentially similar to those of Grahame⁽¹⁴⁾.

Results of the impedance at a platinum electrode in acid solution in the presence and absence of hydrogen are confusing, although the expected marked dependence of the impedance upon the frequency of the perturbing A.C. signal is shown. These preliminary results indicate an expected change in the electrode capacity on the formation of oxide, but do not show a well defined capacity peak in the region of the theoretical hydrogen electrode potential as would be expected from a rapid reversible electrochemical reaction. Further work to clarify this is being carried out. It is felt that better control of the potential of the electrode is needed and true potentiostatic control will probably have to be used.

An apparatus for the passage of a controlled constant current has been built. This is a single step device at the present, no experimental arrangement for the separate charging of the double layer being incorporated. (A double pulse). The changing potential is recorded on an oscilloscope which itself triggers the current pulse internally, so that the pulse begins at a period of one millisecond after the oscilloscope trace begins.

Results obtained for hydrogen on platinum in acid and basic solutions for the reactions





(Stockholm convention)

indicate the primary kinetic control expected, however, final conclusions from more sensitive measurements are being obtained.

(4) Electrode Dynamics Within Cylindrical Catalyst

The dynamics (combined mass-transfer rates and reaction rates) within a typical fuel cell pore are being examined both analytically and experimentally employing a small diameter (1-10 mil i.d. transition element tube). The relative importance of the competing processes of diffusion and chemical kinetics under a variety of physical conditions is to be established.

(a) Mathematical Analysis of the Dynamics in a Three Phase Electrode

The motivation for the present activity had been to discern any significant electrode polarization resulting from the simultaneous consideration of the following factors: (1) the detailed balance of current being produced at each position along the surface with the transport to and from the surface of each chemical species in the half-cell reaction, and (2) the establishment of conditions along the surface such that the half cell has a uniform electromotive force. The usual treatments on concentration and diffusion polarization do not include the simultaneous consideration of these factors.

The goal of the analysis is to predict the behavior of a single pore in a gas diffusion electrode by a description which contains a minimum of physical considerations and adjustable parameters. It is possible to have a preliminary check for the analysis by testing to see whether it indicates the small "reaction zone" for gas diffusion electrodes implied by Justi⁽²⁰⁾ and recently experimentally demonstrated by Weber et al.⁽²⁴⁾ and by Will⁽²⁵⁾.

(24) Weber, H.C., et al., J. Electrochem. Soc., 109, 884.

(25) Will, F.G., ibid, 110, 145.

1) Assumptions and basic equations.

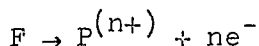
In contrast to the theoretical analysis of Will⁽²⁶⁾ and that of Justi⁽¹⁾, the basic equations used for a description are those governing the motion of reactant and product species in the electrolyte. The approach used is that

(a) the transport mechanism of the reactant to the catalytic surface contacted by electrolyte is by diffusion through the electrolyte,

(b) the motion of the chemical species in the electrolyte can be described by Fick's diffusion equation for continuous media,

(c) there is no appreciable migration of chemical species on the surface or in a thin film on the surface.

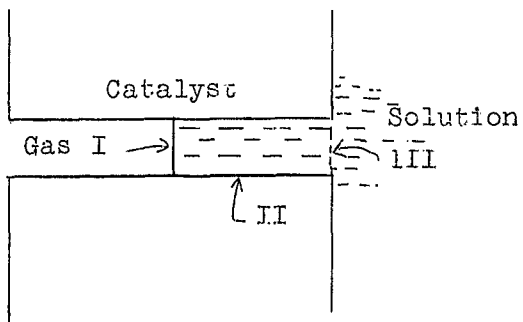
The initial analysis is for a simple half-cell reaction of the type:



where F = reactant

$P^{(n+)}$, hereafter, P = ionized product.

The reaction is to take place only on the catalytic surface (surface II below) contacted by electrolyte. The basic equations are to govern the concentrations of F and P in the electrolyte contained between the interface (I), the catalyst surface (II), and the end of the pore (III). A cross section of the pore is shown below:



(26) Will, F.G., *ibid*, 110, 152.

The current-versus-polarization curve for steady operation is the behavior desired from this analysis. For steady state, the diffusion equations are:

$$\Delta^2 (F) = 0$$

$$\Delta^2 (P) = 0$$

where (F) = concentration of F in the electrolyte
 (P) = concentration of P in the electrolyte
 Δ^2 = La Placian (three dimensional)

The current is obtained via the solution to equation A. The flux of F into the catalyst surface is the local current density (in equivalents). Integration of the flux over the surface gives the total current. The polarization is introduced through a boundary condition.

2) Boundary Conditions.

The end boundary conditions for equation A are:

(3) there is no flux of F through the far end of the pore (III); and (4) the concentration of F at the interface is that which is in equilibrium with the gas. The end boundary conditions (B.C.) for equation B are: (5) there is no flux of the ion P into the gas phase, and (6) the concentration of P at the far end of the pore (III) is that of the bulk electrolyte. These boundary conditions are readily expressed in terms of (F) , (P) , their gradients, and their diffusion coefficients.

The two differential equations are made to influence each other by the previously mentioned factors (1) and (2). The detailed balance of current with the transport of chemical species is B. C. (1), which for this description states that the flux of F into the catalyst surface equals the flux of P into the electrolyte at each position along the surface. The second factor, that the half-cell has a uniform e.m.f. is less obvious; it states that at steady state, concentration cells can not exist within the pore. This statement is not to mean that a uniform current density exists

along the pore wall, but that there is no tendency for F to be oxidized at one position on the pore wall and P to be reduced to F at another position. How this factor is expressed as a boundary condition is discussed in the next two sections.

The first approach to B.C. (2) was to hypothesize that once F reaches the catalyst it is converted to P and returned to the solution very rapidly (in comparison to the diffusion processes) and that the Nernst expression, using the concentrations of F and P adjacent to the catalyst, indicates the electromotive force. For the e.m.f. to be uniform, then the ratio of the concentrations of F to P along the surface must be constant; however, the concentration of each is a function of position along the surface. One then obtains a polarization-vs-current relationship by prescribing different values of this ratio and then determining the current from the solutions to equations A and B.

The solution to the differential equations using these six B.C. looked encouraging; however, it is expressed as an infinite series and it does not give converging values for the current densities. Examination of the equation indicated that if any other resistance to the overall process would be added, converging values for the current density would be obtained.

Several different types of resistances might be added. Those examined were:

- 1) a resistance for the reactant gas to enter the solution at the interface.

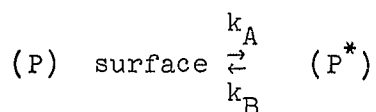
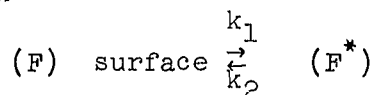
- 2) a catalytic parameter k_1 (the inverse of a resistance), which is a measure of the ability of the catalyst to convert F in solution at the surface to the activated state of F on the catalyst surface, called F^* . The parameter k_1 would then be a measure of the "pull of the catalyst".

- 3) similarly, a catalytic parameter k_A , which is a

measure of the ability of the catalyst to convert the activated state of P on the surface, P^* , to P in solution. The parameter k_A is then a measure of the "push of the catalyst".

The effect of adding a resistance to the gas entering the solution at the interface is to alter B.C (4). It was ascertained that the addition of this factor gives convergent values for the current density. However, a qualitative description would require a highly involved mathematical exercise, and intuition indicates that other factors may be more important. After the analysis is applied to the experimental data, this factor can be appraised from kinetic theory.

Currently, catalytic parameters k_A and k_1 are incorporated into B.C. (2). The justification for and implications of using these parameters will be included in a detailed report later this year. The addition of these parameters into B.C. (2) follows. It is assumed that the conversion of F^* to P^* is rapid, and that the Nernst equation applies to these species. For a uniform e.m.f. the ratio of F^* to P^* must be constant along the catalytic surface, though again (F^*) and (P^*) vary with position. The polarization is determined by setting this ratio. Consideration of reverse mechanisms to k_1 and k_A as follows:



allows one to express B.C. (2) in terms of (F) , (P) , their gradients, k_A , k_1 , and the diffusion coefficients. Convergent values of current densities are obtained for every position along the surface if either k_1 , k_A , or both are considered along with the diffusion coefficient of F.

In the early stages of the development a numerical solution was obtained using crude numbers for k_1 and the other parameters. The current density was convergent everywhere, and the effective catalyst area was found to be very small and adjacent to the interface.

The most interesting part of the analysis is that both k_A and k_1 cannot be neglected. If the analysis is an accurate model, then an experiment such as those of Will⁽³⁾ must be influenced also by one or both of these parameters. Moreover, the polarization curve must be sensitive to the values of the catalytic parameters, since a convergent solution is not obtained by ignoring them. For the case where k_1 is the controlling catalytic parameter, the shape of the predicted polarization curve is radically different from the one where k_1 can be neglected and only k_A need be considered as the catalytic parameter. If both k_A and k_1 are relevant at low polarizations (0.2V) then as the polarization is increased the influence of k_A is rapidly diminished and values for both parameters may be obtained. The analysis indicates that in addition to the diffusivity of the reactant through the electrolyte, at least one other rate-controlling mechanism must be included for gas diffusion cells. (The diffusivity of P was eliminated in the course of the mathematical solution by approximations of the type $1/(1-X) = 1 + X$ if X is small. Thus, it was not eliminated from the solution a priori).

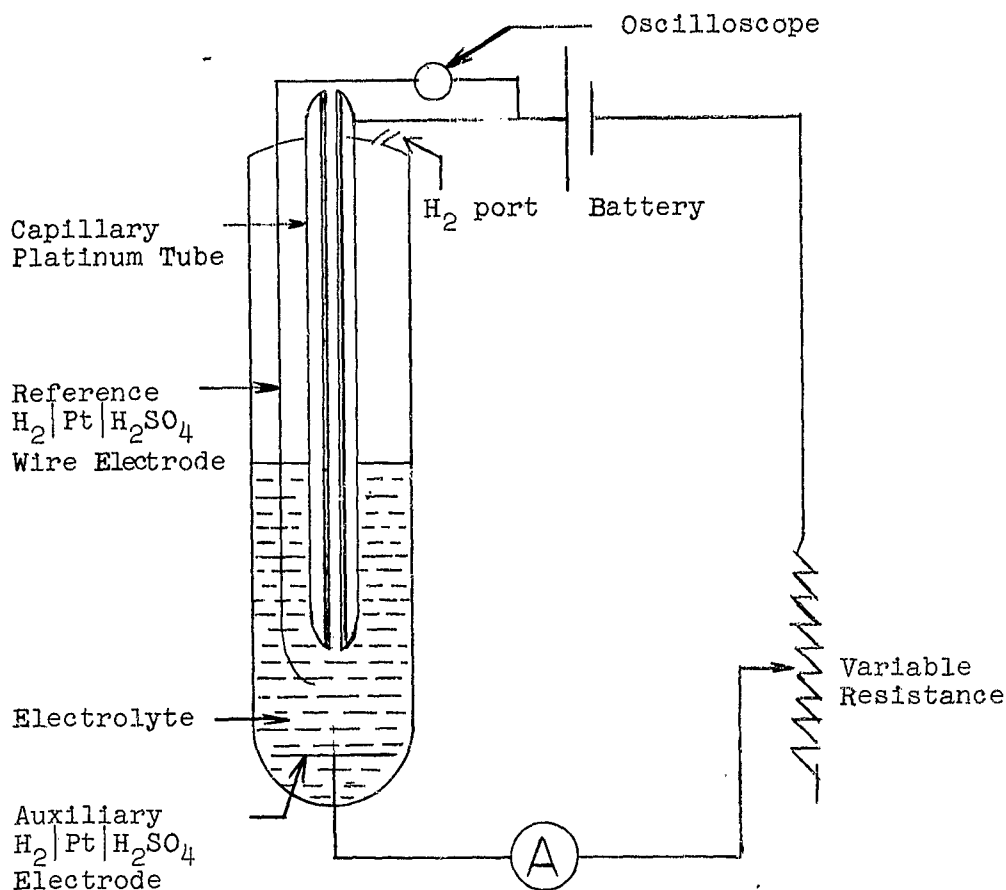
The proposed research is a slight modification of the theory to describe $H_2 \rightarrow 2H^+ + 2e^-$, and a thorough check of the theory for data on the hydrogen half cell. The theory contains two independent parameters, the solubility of the reactant and its diffusion coefficient in the electrolyte, and it contains two arbitrary parameters k_1 and k_A . Thus, to account for the ease in fitting any curve with data is necessary.

If the theory is successful, the proposed research would include the initiation of experimental studies on fuel-cell systems from this point of view. If not successful, careful checking with data is necessary to indicate the direction for revision.

The advantages of the model are that it is based on simple considerations, and therefore may provide a good basis for the schematic description of gas diffusion electrodes. It also indicates that a gas diffusion type electrode (where the reactant-electrolyte interface contacts the catalyst) provides a sensitive test for indicating the type of catalytic behavior which, along with the reactant diffusion coefficient, are the controlling factors.

(b) Experimental Study of the Dynamics in a Three-Phase Capillary Electrode

A single capillary platinum tube 40 μ in inner diameter has been chosen for the studies to simulate behavior in a single pore of a complicated multi-porous electrode. The behavior of the porous electrodes designed by Justi⁽²⁰⁾ was explained assuming a three-phase system in a porous electrode might be elucidated. Such studies should supplement the experiments of Justi and Will^(25,26), who studied the electrochemical effect of meniscus position on submerged rods. The reactant now being studied is gaseous hydrogen reacting in a 1N H₂SO₄ aqueous electrolyte. The apparatus shown schematically below consists of a platinum capillary (40 μ I.D.) sealed in pyrex and effectively a galvanostatic method with an external e.m.f. source is being employed.



Current-voltage-time relationships for various tube-pore diameters and meniscus heights in the tube are being obtained for several conditions: (1) H_2 saturating whole electrolyte system, (2) H_2 suddenly exposed to meniscus with no H_2 in electrolyte, (3) inert gas over electrolyte which is saturated with H_2 . The total internal wetted area of the platinum surface is varied by changing the immersion depth. The meniscus height is determined by probing through the top of the platinum tube with a fine steel wire insulated everywhere but at its tip, the meniscus being indicated by electrical continuity. To date the apparatus is completed and current-voltage measurements are underway.

III. THERMOELECTRICITY

(a) Materials Research

The major activity in this report period has concerned efforts to elucidate the precise range of stability for the δ phase and the band structure of the δ phase in the Ag-Sb-Te system. A previous technical report has described the technique developed to obtain single phase material. The exact limits of stability of the δ phase are not yet known. In addition, other investigators have observed a eutectoid decomposition.

In an effort to resolve these questions several samples of various composition (initially single phase δ) were annealed for 900 hours at 300°C and the resulting material examined metallographically and with x-rays to determine the presence of additional phases. In no case was the presence of two new phases observed which would occur in the case of a eutectoid decomposition. Nucleating agents were added to some samples in an effort to overcome any problems in nucleation of eutectoid products, however, the observations were always similar. In all cases a small amount of an additional phase (usually Sb_2Te_3) was observed. In one sample, only a small amount of Sb_2Te_3 was observed to form. This sample is being analyzed chemically in order to corroborate the stable δ composition.

Considerable work has been done to determine the band gap for the δ phase using Hall effect studies and absorption spectroscopy. Hall apparatus was refined in order to measure the low values of the Hall coefficient. All samples observed to date show similar behavior: very slight increase in R_H with temperature (from 77°C to 300°K) with values about $10^{-2}\text{cm}^3/\text{coulomb}$. The resistivity increases with temperature over the range 77°K to 300°K. The calculated carrier concentrations are generally around $10^{19}/\text{cm}^3$.

In an effort to determine the band gap optically, several samples were analyzed using a Perkin-Elmer Model 13 Spectrometer. Considerable difficulty arose in thinning samples by lapping techniques. Finally, a number of samples were thinned to 25 microns, which is the limit to which this material can be thinned using conventional lapping techniques. Using these samples, no transmission was observed out to 35 microns, probably due to free carrier absorption.

Efforts to utilize resistivity and Hall measurements to determine the thermal band gap and optical absorption to determine the optical band gap are currently inconclusive. The indications are that either overlap exists or a very small gap exists. Possible solutions to this problem currently under evaluation are: measurement of Hall coefficient down to liquid helium temperatures in order to measure a smaller thermal gap; and preparation of absorption samples consisting of powder of δ imbedded in KBr in order to have a thinner effective thickness.

The personnel active in the program doing this research period were Professor D. A. Stevenson, D. Bell, R. A. Burmeister, R. A. Reynolds and T. Tromblee.

(b) Measurements of Thermoelectric Properties

Measurement of Seebeck Coefficient

The apparatus for measuring Seebeck coefficients and electrical resistivity at elevated temperatures has been redesigned and the new apparatus has been built. Modifications made were to provide additional instrumentation of the sample in order to determine the magnitude of possible errors resulting from thermoelectric effects between the sample and the thermocouple.

Thermal Diffusivity Measurements

The modifications of the electronic equipment to which reference was made in the previous report has been carried out. The results of this modification have been satisfactory. Consistent results of the thermal diffusivity

of both N-type and P-type lead telluride have been obtained at room temperature. It was found advantageous to plate the back face of the sample in order to short out extraneous signals which distort the temperature history curves. These signals result from the thermoelectric character of the samples.

Typical results are as follows:

1. P-type lead telluride, 0.25" in diameter
0.052" thick, plated with silver on the back
face:

$$\alpha = 2.4 \times 10^{-2} \text{ cm}^2/\text{sec}$$

2. N-type lead telluride, 0.25" in diameter,
0.072" thick, no plating:

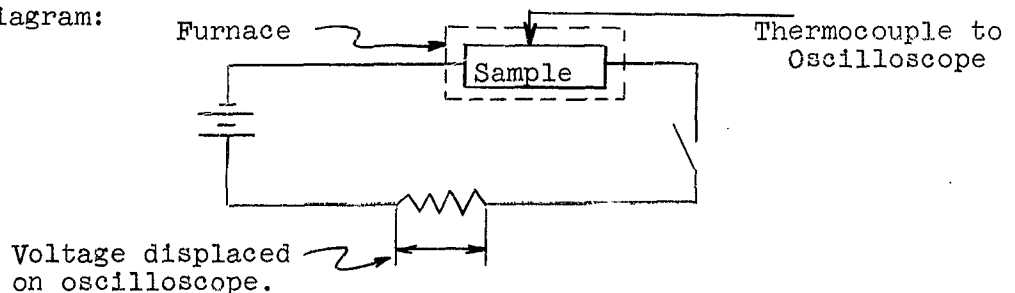
$$\alpha = 2.2 \times 10^{-2} \text{ cm}^2/\text{sec}$$

The furnace and associated apparatus designed for measuring thermal diffusivity at high temperatures have been assembled and tested.

Measurements of Specific Heat

A promising method of determining the specific heat of electrical conductors and semiconductors was conceived. The method is based on a short duration experiment so that the usual problems of heat transfer may be neglected.

The apparatus is shown schematically in the following diagram:



Closing the switch, a current I flows through the sample so that its temperature rises by 3° to 5°F in a few milliseconds.

Consider the energy equation for an element, dx , at center of the sample:

$$\rho c A dx \frac{dT}{dt} = I^2 \frac{1}{\sigma} \frac{dx}{A}$$

where t is time and σ is the electrical conductivity. Then

$$C = \frac{I^2}{A^2} \frac{1}{\rho \sigma} \frac{1}{\frac{dT}{dt}}$$

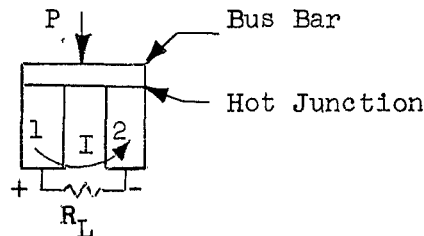
I may be inferred from the voltage drop across the resistor, σ can be measured. Thus C is found by observing the slope of the temperature-time trace on the oscilloscope.

When D.C. is used, care must be taken to perform the temperature measurement during a short period to prevent the influence of the Peltier effect at the junctions.

Most of the last reporting period has been spent on experimentation in order to determine the characteristic currents, duration of measurement and data recording method.

(c) Transient Behavior Thermoelectric Generators

Study centers on the following problem: a thermoelectric generator, shown in Figure 1, is initially at temperature T_1 . Beginning at time $\theta = 0$, the hot junction bus bar receives a constant power input P , while the cold junction temperature is held constant at T_1 .



Internal Resistance = R_1 ohms
Load = R_L ohms
Power Unit = P watts

Figure 1

Non-dimensionalization of the governing equations for device response shows that the device response, in terms of the hot junction temperature or the electrical current I depends upon only four dimensionless parameters: a thermal capacity ratio, $C^* \triangleq (C_{\text{bus bar}}/C_{\text{legs}})$; a dimensionless power input P^* , a dimensionless initial temperature T_1^* , and a load ratio, $m \triangleq (R_L/R_1)$.

Figure 2 shows some qualitative response curves for a given C^* . Note that the open circuit ($m = \infty$) response is

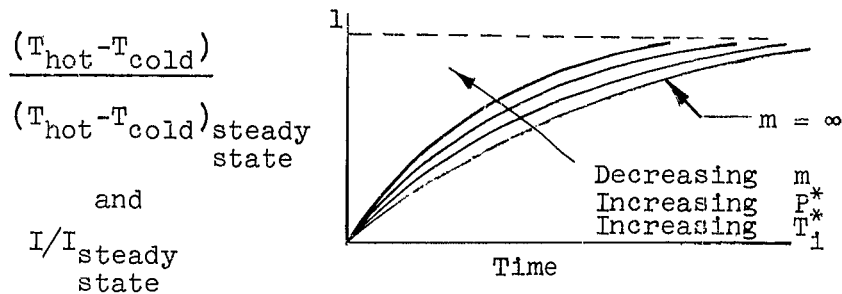


Figure 2

common for all P^* and T_1^* , and is the slowest response. Figure 3 shows qualitatively the differences between any response curve and the open circuit response curve.

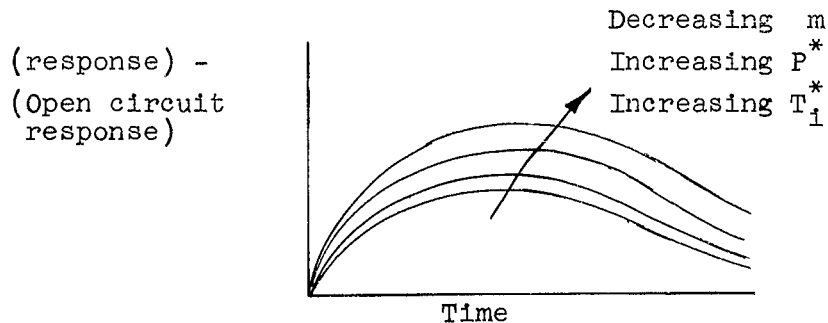


Figure 3

Experimental work aimed at verifying the predicted responses consumed the reporting period. The data from 32

open circuit runs and 14 runs at one electrical loading show agreement with finite-difference calculations to within 0.01 for the total response (that is, to within 1% of the steady state value) and to within about 0.003 for the difference between the closed circuit and the open circuit curves.

Work during the next reporting period will be devoted to examining other cases of the load ratio m . Variations in response with the power P^* and the initial temperature T_1^* are smaller than the variations with m and probably cannot be found experimentally with the present equipment.